

SYNTHESIS OF STEREOISOMERIC - METAL COMPLEXES USING
PHASE-TRANSFER CATALYSIS AND PHOTOCHEMICAL TRANSFORMS
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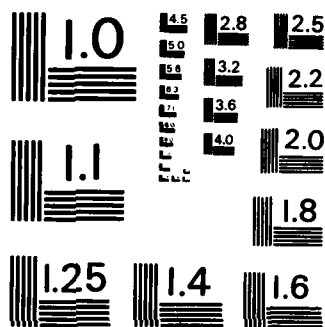
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NO. 128

SYNTHESIS OF STEREOISOMERIC - METAL COMPLEXES
USING PHASE-TRANSFER CATALYSIS AND
PHOTOCHEMICAL TRANSFORMS



UNITED STATES NAVAL ACADEMY
ANNAPOLIS, MARYLAND
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The reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ (where $\text{X} = \text{Br}, \text{Cl}, \text{I}$) complexes with allyl derivatives under phase transfer conditions have been examined. It has been determined that product identity and selectivity are sensitive to the nature of the halide ligand on the metal center, the rate and manner of addition of reactants, the polarity of the organic solvent and the leaving group on the allyl ligand. These studies suggest that two mechanisms are operative in the formation of σ - and π -allyl complexes. Analogous reactions with $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ have been carried out and demonstrate that ruthenium shows a strong preference for the production of π -allyl complexes with little dimeric by-product being formed. Preliminary studies of the $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ with crotyl bromide indicate that four π -crotyl complexes are being formed.

Exploratory studies on the synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CNCH}_3)_2(\text{C}_2\text{H}_4)] \text{PF}_6^-$ complexes where $\text{M} = \text{Fe}$ or Ru were conducted. It was found that the introduction of ethylene by the photochemical decarbonylation of the bisisocyanide metal species $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CNCH}_3)_2(\text{CO})]^+ \text{X}^-$ is complicated by photochemical decomposition of the olefin product. Synthetic modifications have been proposed with the olefin product. Synthetic modifications have been proposed with the expectation of circumventing this problem.

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Synthesis of Stereoisomeric - Metal Complexes Using
Phase-transfer Catalysis and Photochemical Transformations

A Trident Scholar Project Report

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ABSTRACT

Cyclopentadienyl carbonyl complexes of iron and ruthenium have been shown to have broad applications in organic synthesis. The viability of these complexes as intermediates is dependent upon convenient and rapid synthetic routes for their preparation. This research has primarily been directed towards the extension of phase-transfer techniques to the preparation of iron and ruthenium allyl and crotyl complexes. In addition, the synthesis of iron and ruthenium olefin complexes by photochemical techniques has been investigated. <

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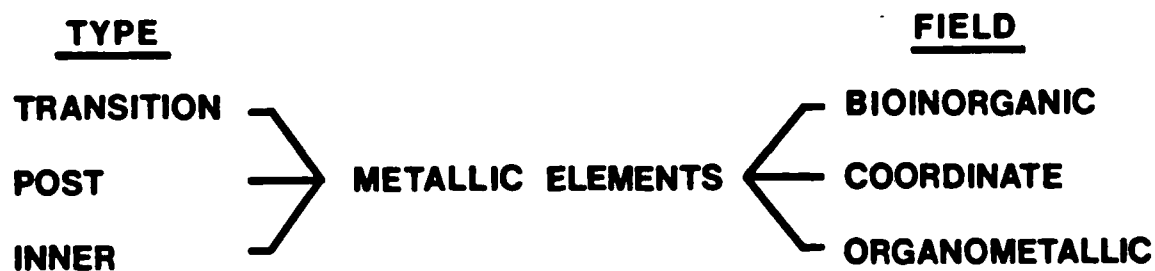
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CHAPTER I

AN INTRODUCTORY SURVEY

Inorganic chemistry has recently been defined as "the experimental investigation and theoretical interpretation of the properties and reactions of all the elements and of all their compounds, except the hydrocarbons and most of their derivatives."¹ This large field of chemistry is indeed extremely diverse and can be subdivided into three main areas²: (a) the study of nonmetal systems, including boron, silicon, phosphorous and the halogens, (b) the study of the classical ionic salts such as those of the alkali and alkaline earth metals ("light metals") and (c) the study of the metallic elements, including the transition metals, the post-transition metals and the inner-transition metals (Table I-1).³ The study of the chemistry of the transition elements can then be further subdivided into three fields: (a) bioinorganic chemistry, (b) coordination chemistry and (c) organometallic chemistry (Scheme I-1).



Scheme I-1

Periodic Table of the Elements

NONMETALS

1	H	1.008
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LIGHT METALS

3	Li	6.94	4	Be	9.01
11	Na	22.99	12	Mg	24.31
19	K	39.10	20	Ca	40.08
37	Rb	85.47	38	Sr	87.62
55	Cs	132.91	56	Ba	137.34
87	Fr	(223)	88	Ra	226.03

TRANSITION METALS

5	B	10.81	6	C	12.011	7	N	14.01	8	O	16.00	9	F	19.00	10	Ne	20.18
13	Al	26.98	14	Si	28.09	15	P	30.97	16	S	32.06	17	Cl	35.45	18	Ar	39.95
31	Ga	69.72	32	Ge	72.59	33	As	74.92	34	Se	78.96	35	Br	79.90	36	Kr	83.80
49	In	114.82	50	Sn	118.69	51	Sb	121.75	52	Te	127.60	53	I	126.90	54	Xe	131.30
81	Tl	204.37	82	Pb	207.19	83	Bi	208.98	84	Po	(209)	85	At	(210)	86	Rn	(222)

POSTTRANSITION METALS

INNER TRANSITION METALS

58	Ce	140.12	59	Pr	140.91	60	Nd	144.24	61	Pm	(145)	62	Sm	150.35	63	Eu	151.96	64	Gd	157.25	65	Tb	158.93	66	Dy	162.50	67	Ho	164.93	68	Er	167.26	69	Tm	168.93	70	Yb	173.04	71	Lu	174.97
90	Th	232.04	91	Pa	(231)	92	U	238.03	93	Np	(237)	94	Pu	(244)	95	Am	(243)	96	Cm	(247)	97	Bk	(249)	98	Cf	(249)	99	Ea	(254)	100	Fm	(257)	101	Md	(258)	102	No	(259)	103	Lr	(260)

Lanthanides

Actinides

Numbers in parentheses: available radioactive isotope of longest half-life.

Table I-1

Bioinorganic chemistry is one of the more rapidly developing areas of inorganic chemistry and is the study of metal complexes incorporated in living systems. A major effort in this area concerns modelling studies of metal-containing enzymes. This is done to understand the role of the metal in living systems.

Coordination chemistry is the study of the chemistry of adducts formed when metals in higher oxidation states ($> +2$) are bound to inorganic and/or organic ions or molecules. Representative examples of such species (referred to as ligands) are amine (NH_3), water (H_2O) and the halides (F^- , Cl^- , Br^- , I^-). One common characteristic of such complexes is that the ligands donate an unshared pair of electrons to the ionic metal center to form a coordinate covalent bond. An example of such a species is one of A. Werner's cobalt salts,⁴ $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. Synthetic and structural determination studies of such compounds are conducted in an effort to gain insight into the factors affecting their spectroscopic, magnetic and thermodynamic properties.

One of the most interesting and important areas in which modern inorganic chemists are involved is the study of organometallic chemistry. Organometallic compounds may be simply characterized as those in which a metal, usually in a low valence state (-1 , 0 , $+1$), is bonded through carbon to an organic molecule, radical or ion.

The earliest example of an organotransition metal compound, $\text{K}^+ [(\text{C}_2\text{H}_5)_4\text{PtCl}_3]^-$, was reported in 1831 by W. C. Zeise,⁵ although the nature of this compound was not fully appreciated until the 1950's. Despite this early start, few additional studies of organometallic compounds were reported in the 1800's with E. Frankland's⁶ synthesis of alkyl-zinc derivatives in 1848 being the exception. In the 1890's, it was found that many transition metals react with CO to form metal carbonyl compounds. However, no reactions with these metal species were pursued until much later.

In the early 1900's, interest in organometallic chemistry shifted to the light metals with the discovery of alkylmagnesium compounds by V. Grignard,⁷ to whom the Nobel Prize was awarded in 1912. As these compounds could be directly applied to the synthesis of organic compounds, their study dominated organometallic chemistry for the next 40 years.

Few significant discoveries were made in organotransition metal chemistry until 1950. Two groups of workers, T. J. Kealy and P. L. Pauson,⁸ and S. A. Miller, et al.,⁹ simultaneously reported the synthesis of a uniquely stable compound of cyclopentadiene and iron. The structure of this compound which was proposed by Kealy and Pauson (1) was thought to have a single-bond structure in which the C_5H_5 moieties are bonded directly to the iron center. The following year, G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward¹⁰ suggested that this structure was incorrect and proposed a π -bonded arrangement (2) as depicted in Figure I-1.

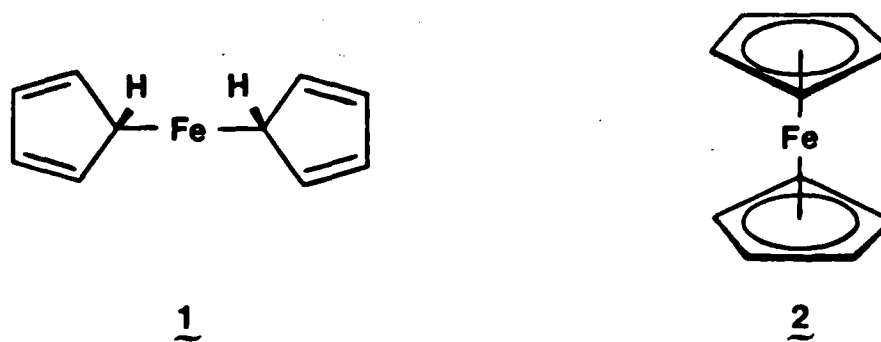


Figure I-1 Proposed Structures of Ferrocene

In order to understand clearly the interactions of the ligands with the metal center in organometallic complexes, it is necessary to be familiar with the spatial distributions of the d atomic orbitals of the metal. The usual graphical representations of these orbitals is shown in Figure I-2.¹¹

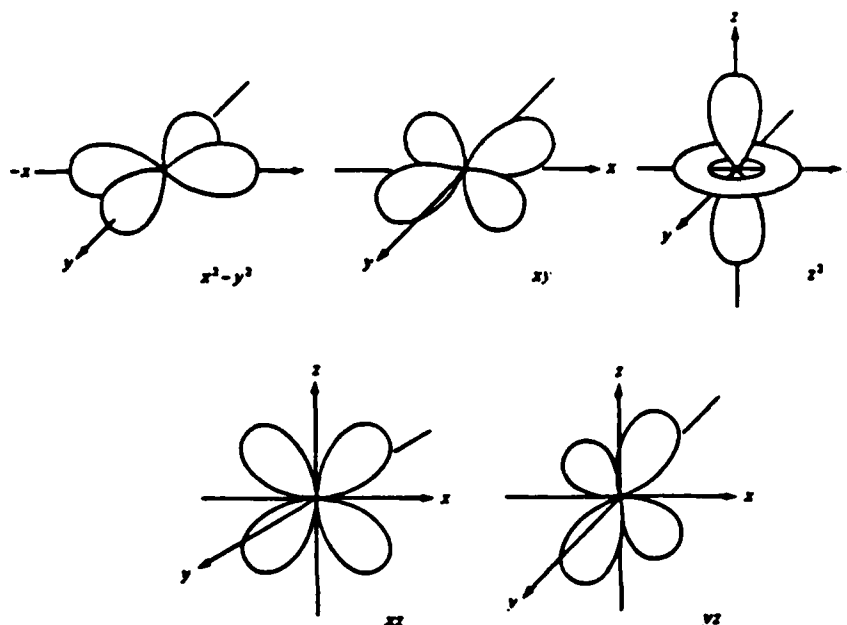


Figure I-2 Spatial Arrangement of the Five d Orbitals

Overlap between the atomic orbitals of the carbon-containing ligands with these d orbitals of the metal can be categorized into two classes. The first of these is referred to as sigma-bond donation (σ) in which the carbon atom of the ligand acts as a simple two-electron donor. This results in the formation of a very strong covalent bond between the filled p orbitals of the carbon and an empty d orbital of the metal center. This is often referred to as "end-bound" or longitudinal bonding and can best be depicted as shown in Figure I-3.¹²

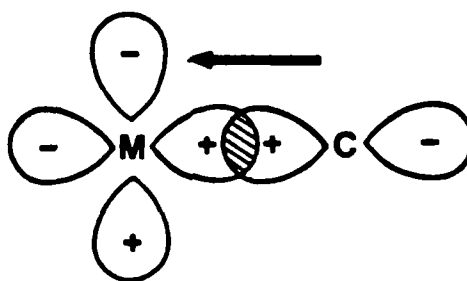


Figure I-3 Ligand-to-Metal σ Bonding

The second class is called π -bond formation (π) in which two or more carbon atoms of the ligand act as a multielectron donor to the metal. As a result, a "side-bound" or transverse bonding¹² arrangement results due to the overlap of an empty d atomic orbital of the metal with the π -orbitals of the carbon system. Metal-to-carbon π -bonding is formed when unsaturated ligands such as olefins, aromatics and their derivatives are bound to metal atoms. Figure I-4¹² illustrates this case for a simple metal-to-olefin interaction, as found in Zeise's salt. Figure I-5³ depicts the more complicated interaction between a metal and the delocalized aromatic ring of the cyclopentadienyl ligand, C_5H_5 .

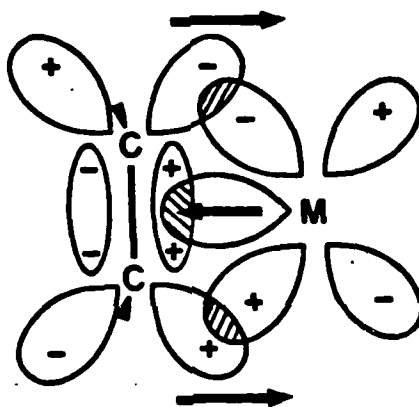


Figure I-4 Ligand-to-Metal π -Bonding in Olefinic Moieties

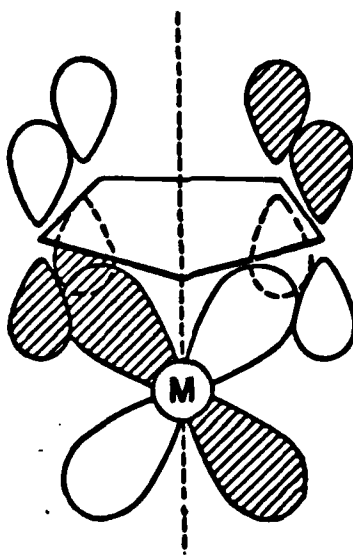


Figure I-5 Ligand-to-Metal π -Bonding in Aromatic Moieties

An additional aspect of bonding which must be considered is the accumulation of unacceptable electron density on the metal atom as a result of the implied one-directional flow of electrons from the carbon atom to the metal. When possible, the metal attempts to reduce this build-up of negative charge concentration, by shifting some electron density back to the ligand. This is possible only if the ligand has low-energy vacant orbitals of the correct shape and orientation to form π -bonds with the filled metal d orbitals. This phenomenon is referred to as "back-bonding,"¹³ which is synergistic in nature due to the resulting cyclic flow of electron density. While the degree of back-bonding is highly variable and dependent upon the identity of the ligand, the overall effect of this multi-bond mechanism is to produce a very strong ligand-to-metal interaction. Ligands such as CO, CNR, olefins, aromatic systems and other unsaturated organic molecules are referred to as π -acceptors and exhibit back-bonding. The bonding interactions present in metal carbonyl complexes, $M(CO)_n$, are illustrated in Figure I-6¹² as an example of this "back-bonding" concept.

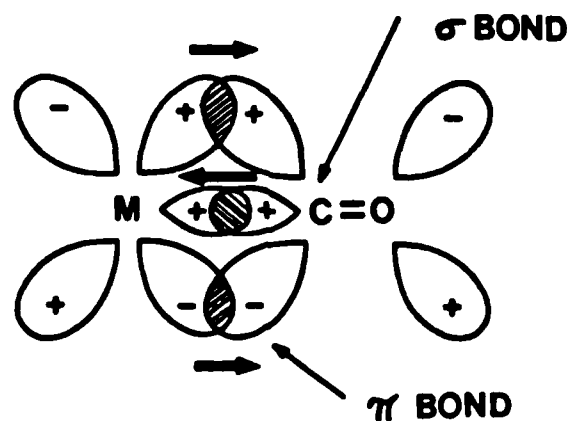


Figure I-6 Ligand \rightarrow Metal σ /Metal \rightarrow Ligand π Electron Flow

The primary evidence for the multiple nature of the M-CO bonds is vibrational spectra. The relative positions of atoms in a complex are not locked but instead fluctuate continuously as a consequence of several vibrational modes. For simple molecules, such as that shown in Figure I-7,¹⁴ these modes include stretching motions along the metal to CO bond axis and bending (or scissoring) of the two CO's about the angle between them. Both of these vibrational modes are affected by variations in the metal-to-carbonyl bonding, but the stretching modes are generally easier to interpret. The energy of these vibrations fall in the range of 1-10 kcal/mole, corresponding to light in the 3-30 μ or infrared region³ (Figure I-8)¹⁵.

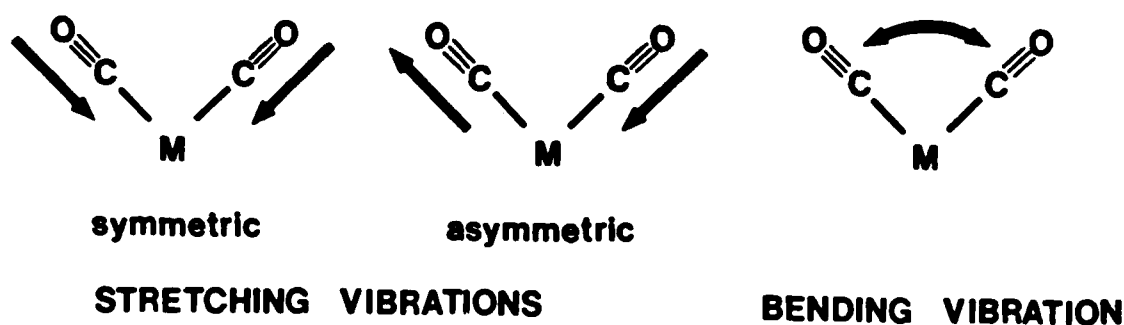


Figure I-7 Vibrational Modes of Metal Carbonyls

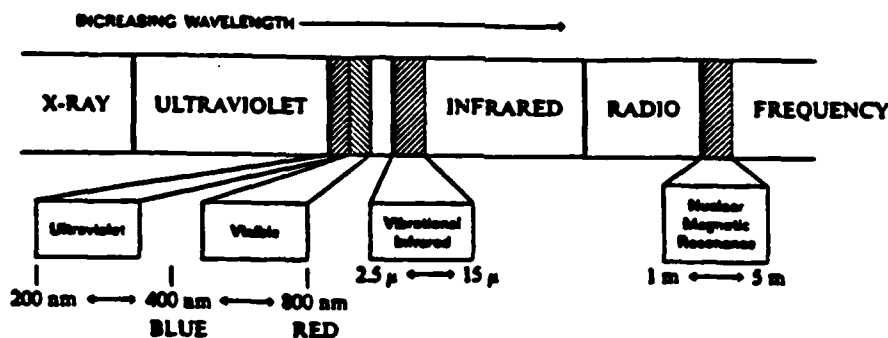


Figure I-8 Electromagnetic Radiation Regions

When infrared light is passed through a sample, those frequencies of light which match the natural vibrational frequencies of the molecule are absorbed. By scanning the infrared region, one produces a spectrum in which the absorptions of light are characterized by bands. Through an analysis of the wavelength of the radiation absorbed, the energy difference between vibrational levels and a measure of the bond character is obtained.

For a series of closely related metal-carbonyl compounds, differences in the carbonyl stretching frequencies are diagnostic of the qualitative changes in metal-to-carbonyl back-bonding. Donation of metal electron density into a vacant carbonyl orbital weakens the bond between the carbon and oxygen. The extent to which the bond is weakened is controlled by the magnitude of the metal-to-carbonyl electron transfer. Since the carbonyl stretching frequency is a measure of the strength of the CO bond, variations in this frequency, therefore, correlate with the degree of back-bonding.

Metal-to-carbonyl back-bonding is sensitive to the identities of the other ligands on the metal. For ligands which are unable to effectively back-bond with the metal, the donation of electron density to the metal results in an enhanced metal-to-carbonyl back-bonding. In this way, the electron donating/accepting abilities of a variety of ligands can be ascertained. In addition to its utility in determining the nature of the M-CO bonding, infrared spectroscopy is a powerful tool for monitoring reaction mixtures and product identification.

A second spectroscopic technique of considerable importance in the structural determination of organometallic species is Nuclear Magnetic Resonance Spectroscopy (NMR)¹⁶. This technique provides a method of probing the electronic environment of selected nuclei, such as ^1H , ^{13}C , ^{31}P , or ^{19}F . Because the electronic environment of a nucleus is directly influenced by the identity of the atoms attached to it, NMR is used as a diagnostic tool for the identification of functional groups in a molecule.

In NMR spectroscopy, a strong magnetic field is applied to the compound under investigation by placing the sample precisely between the poles of a powerful magnet. This is done to create different energy states of the nuclei. By the absorption of electromagnetic radiation of the appropriate wavelength and energy, transitions by the nuclei between the allowed spin states can occur. The energy difference between the two states is proportional to the strength of the magnetic field and corresponds to radiation energies in the frequency range of 0.1 to 300 MHz, the radio-frequency region of the electromagnetic spectrum (Figure I-8). Variations in absorption frequency of the nuclei are observed as a result of the differences between the applied magnetic field and the effective field felt by the nucleus. This difference, due to shielding of the nucleus by adjacent electron density, is referred to as "chemical shift." It is reported in units of parts per million (ppm) relative to a common reference material such as tetramethylsilane, $(\text{CH}_3)_4\text{Si}$, often referred to as TMS.

Minor changes in ligand identity on the metal are easily detected in the observed chemical shift of all nuclei of the same type. For example, in a bromine derivative of iron, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$, the $(\eta^5\text{-C}_5\text{H}_5)$ ring hydrogens resonate as a singlet at 5.1 ppm relative to TMS. By simple substitution of the bromide ligand with a methyl group to form $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$, the cyclopentadienyl ring singlet shifts to 4.6 ppm. In addition, a second singlet is observed at 0.4 ppm for the methyl hydrogens, likewise relative to TMS.

NMR spectra are very useful, and at times critical, in establishing the identities of new organometallic compounds. By an analysis of chemical shifts, line shapes and relative peak heights in the spectrum, important structural information about a complex becomes available.

Earlier in this introduction, it was noted that development of the organometallic chemistry of the light metals was stimulated by the applications of these compounds to problems in organic synthesis. The application of transition metal compounds to organic synthesis, by contrast, was severely limited to the use of finely powdered metals such as platinum for the hydrogenation of olefins.¹⁷ In the 1930's, it was found that several metals served as catalysts for the synthesis of short-chain hydrocarbons from CO and H₂.¹⁸ Other transition metal catalysts were found to be useful in the cracking of crude oils into gasolines and other fuels.¹⁹ In the 1950's Ziegler and Natta²⁰ found that organometallic titanium complexes smoothly catalyzed the polymerization of ethylene and other olefins. This drew attention to the potential of using discrete organometallic compounds rather than bulk metal surfaces, as catalysts which exhibit great efficiency and selectivity. The explosive growth experienced by organometallic chemistry in the 1960's was due in large measure to the interest expressed by both academic and industrial chemists in developing new catalysts and exploring the mechanisms of catalytic activity to guide future work.

In addition to their active uses as catalytic sites for hydrogenation, carbonylation and olefin metathesis, it has been found that organometallic groups substituted onto a molecule may alter the reactivity of these molecules in beneficial ways. Complexation of a metal system with a variety of organic substrates leads to a reduced reactivity towards electrophilic attack and increased reactivity towards nucleophilic attack.

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^+$, "Fp⁺", has been found to act as a convenient group for protecting olefins against electrophilic attack.²¹ As an example, reaction of Fp(isobutylene)⁺ with norbornadiene gives a Fp-olefin complex (3)²² in which one double bond is bound to the iron and the other is free. The free double bond is

susceptible to attack by electrophilic reagents as shown. The mono-olefin can be easily generated by reaction of the metal complex with NaI. (Figure I-9).

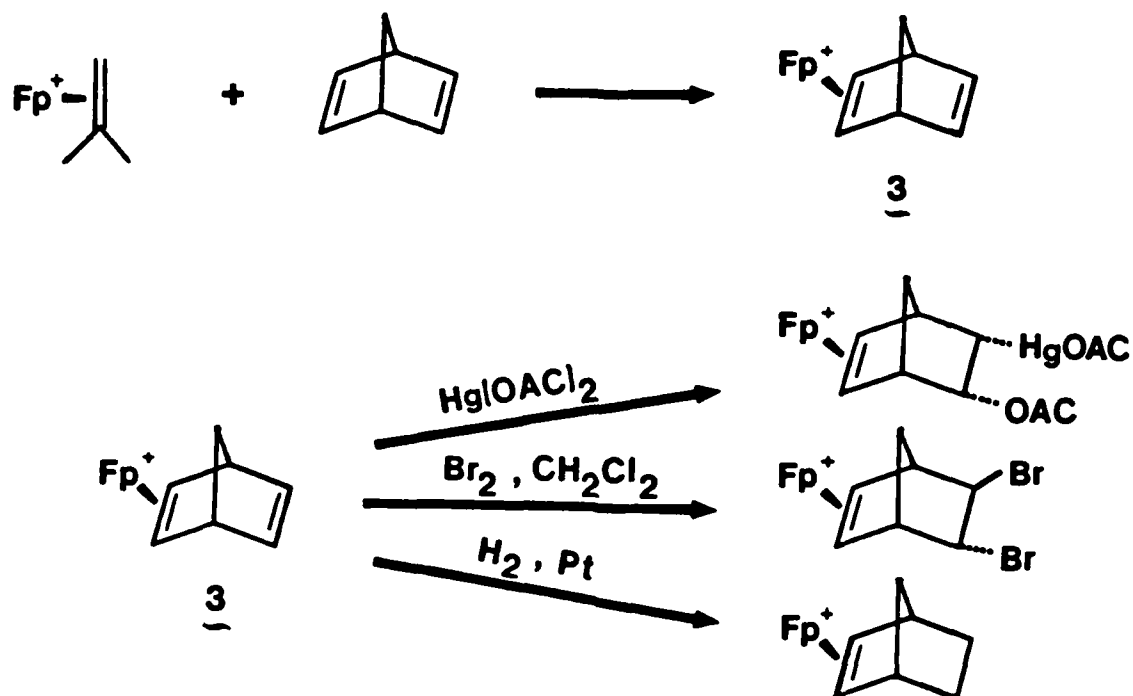
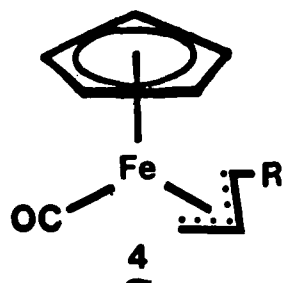


Figure I-9 Protection of Olefins by Fp^+

The interest in using the $(\eta^5-C_5H_5)Fe(CO)_2^+$ moiety as a protecting group has led to the suggestion that this application might be expanded to allyl-substituted molecules such as 4, where R is an organic group.



At the present time, there are few good methods for the generation of allyl metal complexes. As a result, exploratory research in this area has been hampered. It was the purpose of the research described in this paper to develop a new synthetic route to allyl substituted iron and ruthenium complexes and to establish its applicability to a range of organic substrates. While nucleophilic studies of the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^+$ moieties are well-known, investigation of the ruthenium analogue remains virtually unexplored. The second goal of this research therefore was to establish the applicability of nucleophilic additions to ruthenium olefin complexes.

CHAPTER I

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CHAPTER II

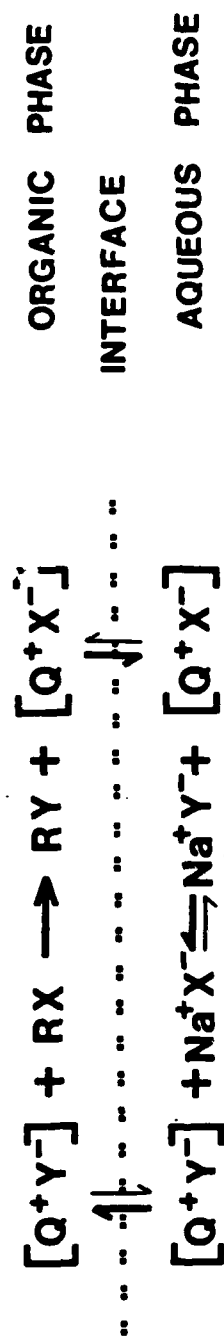
SYNTHESES OF METHYL, ALLYL AND CROTYL DERIVATIVES
OF PENTAHAPTO - CYCLOPENTADIENYL METAL-CARBONYL
COMPLEXES USING PHASE-TRANSFER CONDITIONS

INTRODUCTION

An alternative approach to the conventional synthesis of selected organic compounds during the past decade has been the development of phase-transfer catalysis (PTC). The versatility of such a method is seen in its application in alkylations, eliminations, hydrogenations, isomerizations and oxidation/reduction reactions.^{1,2} In addition, phase-transfer catalysis has been adapted to several industrial processes which produce polymers, pharmaceuticals and intermediates for agrochemicals.³

The introduction of phase-transfer catalysis in the early 1970's was primarily due to the efforts of three independent researchers operating along similar, complimentary lines of thought. While M. Makosza of the Technical University of Warsaw, Poland^{4,5} and A. Brändström of the AB Hassle, Sweden^{6,7} contributed to the development of the process, C. M. Starks⁸⁻¹¹ of Conoco, Inc. of Ponca City, Oklahoma, USA introduced the term "phase-transfer catalysis" and formulated the fundamental mechanism of these reactions. For the general case of nucleophilic substitution, the proposed mechanism is represented in Scheme II-1.² The reaction is carried out in a two-phase system consisting of an organic solvent and an aqueous solution. As a result of the immiscibility of the two phases, an interface is produced. The indicated reactants can be defined as:

Q^+ = cationic portion of a quarternary ammonium salt;
e.g., $[C_6H_5CH_2N(C_2H_5)_3]^+$



Scheme II-1² Phase-transfer Catalysis Mechanism
for Nucleophilic Substitutions

X^- , Y^- = anionic portion of a quarternary ammonium salt such that Y^- is the more lipophilic of the two. Relative scales of lipophilicities have been formulated and the order¹² going from most lipophilic to most hydrophilic ion is:
 $I^- > Br^- > CN^- > Cl^- > OH^- > F^- > SO_4^{2-} > PO_4^{3-}$

RX = organic halide

Kinetic measurements have shown that in solvents of relatively low polarity (i.e., dichloromethane (CH_2Cl_2) or benzene (C_6H_6)) the ion pair, which is indicated by [], is the dominant nucleophilic species as opposed to free ions, which would exist in more polar solvents.¹³ The ion pair is only weakly solvated in nonpolar systems and exhibits an enhanced nucleophilicity, permitting a rapid exchange between Y^- and X^- . Ignoring the problem of the lack of solubility of RX in the aqueous medium, the Y^- ions are too strongly solvated by water to permit effective exchange with X^- .

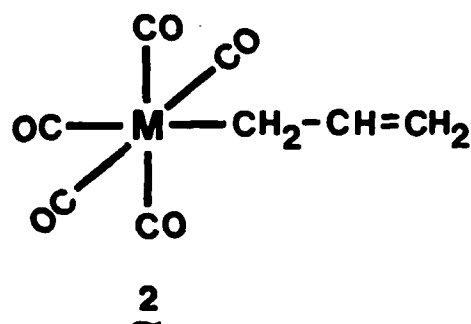
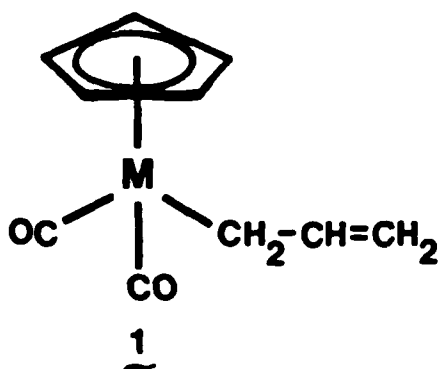
As illustrated in Scheme II-1, the quarternary ammonium salt, $[Q^+Y^-]$, migrates from the aqueous phase to the organic solvent. At this point, the weakly solvated ion pair $[Q^+Y^-]$ undergoes an exchange of the anions with the organic halide RX . The species RY and $[Q^+X^-]$ are therefore formed in the organic phase. The new ion pair generated $[Q^+X^-]$ then migrates across the interface into the aqueous solution. A similar process allows for the exchange of the X^- counterion with the Y^- ion of Na^+Y^- resulting in the regeneration of the active quarternary salt $[Q^+Y^-]$ and an ionic salt by-product. In this manner, a cyclic, catalytic process is maintained. Phase-transfer conditions can also be used to generate reactant intermediates, as will be illustrated below.

In contrast to the standard conditions of a homogeneous reaction, this two-phase catalytic approach permits or accelerates reactions which are normally slow and inefficient or do not occur at all. Therefore, phase-transfer catalysis

has considerable advantages over conventional methods including¹²: elimination of differences in solubilities between reactants, lower reaction temperatures, modified product selectivity, easier purification and work-up and an increased product yield by suppression of side-reactions.

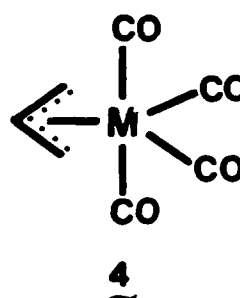
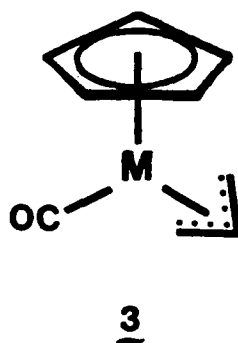
While a significant number of applications of phase-transfer catalysis have been reported in the literature for organic systems, it was not until 1976 that the first organometallic application appeared.¹ The reaction involved the synthesis of a η^3 -allyl derivative obtained through the reaction of $\text{Co}_2(\text{CO})_8$ and $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br}/\text{NaOH}$ under phase-transfer conditions and approached yields of 70-80%.¹⁴

Two major types of allyl transition metal complexes have been identified. The first is a σ -allyl (or $\eta^1\text{-C}_3\text{H}_5$)* in which the terminal carbon is attached to the metal through a single bond. A carbon-carbon double bond in the allyl moiety remains nonbonded to the metal. Examples are $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\eta^1\text{-C}_3\text{H}_5)(\text{CO})_2$ where $\text{M} = \text{Fe}$ or Ru (1) and $(\eta^1\text{-C}_3\text{H}_5)\text{M}(\text{CO})_5$ where $\text{M} = \text{Mn}$ (2).

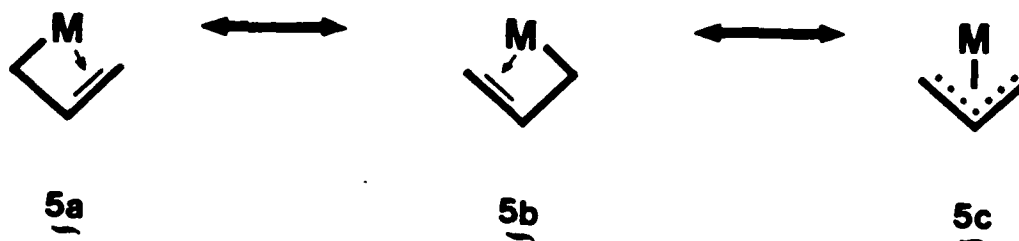


* The notation $\eta^{\#}$ is a shorthand designation used to indicate the number of atoms (#) per ligand formally bound to the metal. The letter η stands for hapto, from the Greek word haptein meaning "to fasten".

A second type of allyl bonding arrangement is the π -allyl (or $\eta^3\text{-C}_3\text{H}_5$) in which the bond between the allyl group and the metal is delocalized and multicentric. Examples are $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})$ where $\text{M} = \text{Fe}$ or Ru (3) and $(\eta^3\text{-C}_3\text{H}_5)\text{M}(\text{CO})_4$ where $\text{M} = \text{Mn}$ (4).



The π -bonded allyl can be seen to arise from the substitution of a metal-bound carbonyl ligand by the allyl $\text{C}=\text{C}$. The allyl species which is produced now formally exhibits resonance as shown by the structures 5a and 5b.

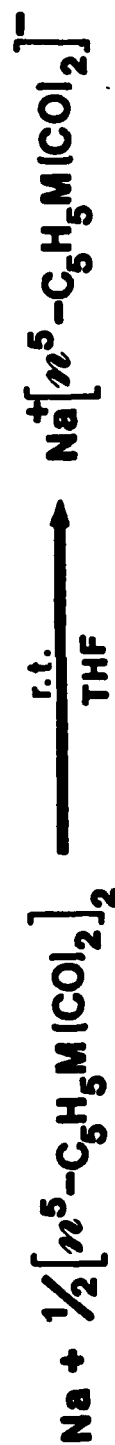


This bonding is best illustrated by the molecular orbital description 5c in which the metal interacts with the bonding π molecular orbital of the allyl moiety. As a result of the delocalization of the electrons in the π -bonded complex, this bonding arrangement is lower in energy and therefore stronger than for the σ -bonded case.

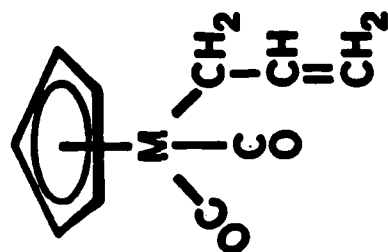
The first synthetic method for the preparation of allyl derivatives with the Group VIII metal iron was developed by M.L.H. Green and P.L.I. Nagy in 1963.¹⁵ Their method involved the initial generation of an iron carbonyl anionic complex, $\text{Na}^+ [(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$, obtained by the reduction of the dimeric species $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ with a 1-2% sodium amalgam (Na/Hg) in tetrahydrofuran. The subsequent reaction of this anionic species with an excess of allyl chloride, $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$, afforded the σ -allyl complex (6) in approximately a 34% yield. The reaction sequence is outlined in Scheme II-2.

The use of sodium amalgam as described in the synthesis above carries with it several difficulties which include the inherent toxicity of mercury and the precautions of handling large amounts of highly reactive sodium amalgam. In addition, side products such as $\text{Hg}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ¹⁶ are formed making this reaction process moderately undesirable and tedious. It is further complicated by the air-sensitive nature of the final allyl-metal product.

In an attempt to overcome these synthetic problems, alternative methods of generating the anionic metal complexes have been adopted. Among these are the reduction of metal carbonyl dimers with (a) heterogeneous reductants such as Na/K alloy¹⁷, (b) potassium hydride, KH ¹⁸, or (c) trialkylborohydrides.¹⁹ While each of these methods offer good to excellent yields of the desired product, all three have some drawbacks in the difficulty of handling dangerous, moisture-sensitive reductants.



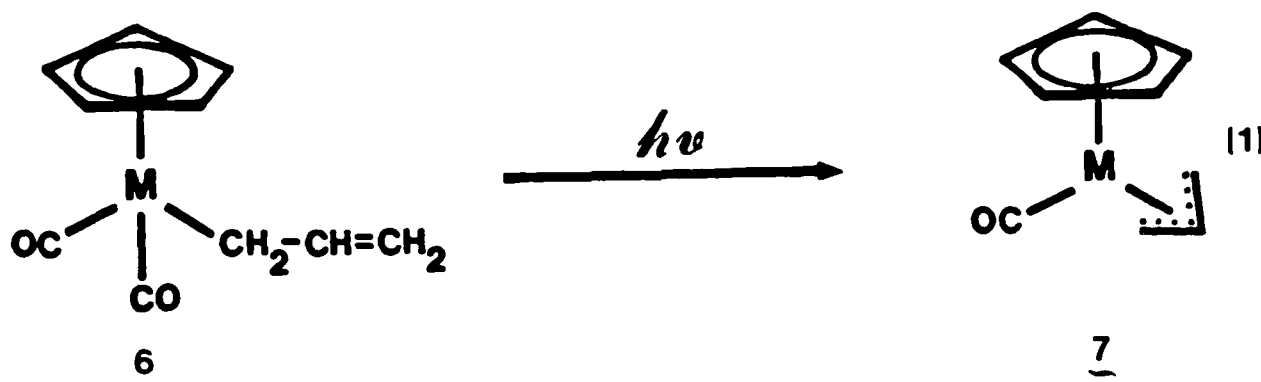
WHERE $\text{M} = \text{Fe, Ru.}$



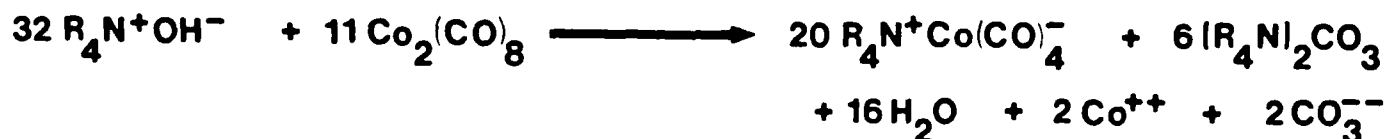
6)

Scheme II-2 Generation of σ -allyl Metal Derivatives Through
a Sodium Amalgam Reduction Process

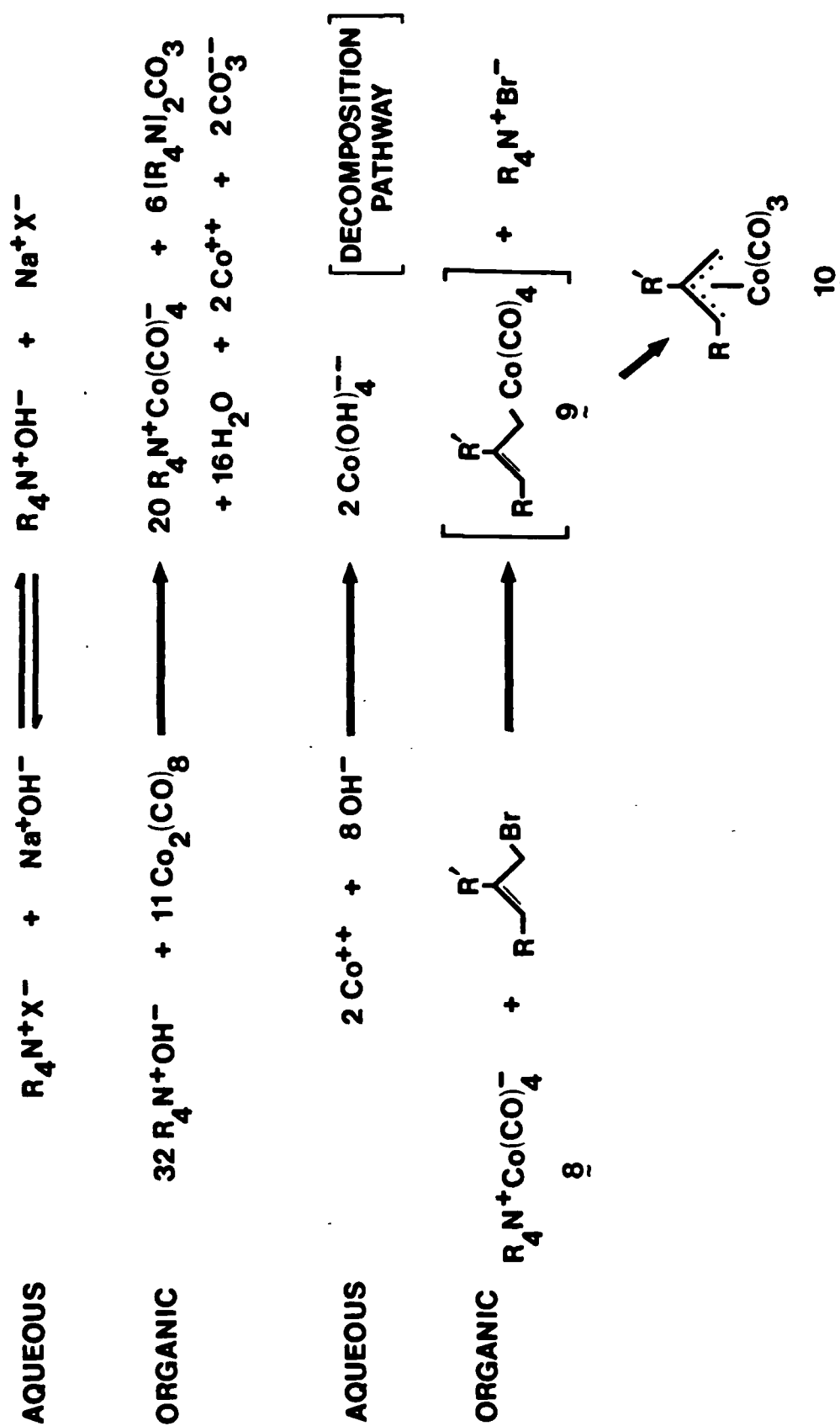
In the synthetic processes outlined above, only the σ -allyl metal complexes are produced. The π -allyl complex (7) can be generated by photochemical decarbonylation of the σ -allyl complex (6) as indicated in equation 1.¹⁵



The most recent method for producing the metal anionic species was reported by H. Alper and coworkers in 1976.¹⁴ It was found that Co(CO)_4^- anion (8) was generated as an intermediate in the reaction of $\text{Co}_2(\text{CO})_8$ with a quarternary ammonium hydroxide under phase-transfer conditions. This reaction can be outlined as:



Subsequent reaction of the reduced cobalt species (8) with $\text{CH}_2=\text{CHCH}_2\text{Br}$ in benzene led to the formation of the η^3 -allyl derivatives (10) in excellent yield, via the η^1 -allyl complex (9) (Scheme II-3).



Scheme II-3¹⁴ Synthesis of a π -allyl] Cobalt Tricarbonyl Complex
via Phase-transfer Catalysis Conditions

As an extension of the phase-transfer catalysis methods proposed by Alper, D.H. Gibson and coworkers²⁰⁻²⁴ recently reported the synthesis of the η^1 - and η^3 -allyl metal complexes ($M = Mn, Mo, Fe, Ru$). In all cases, the metal carbonyl complexes were combined with allyl halides under catalytic conditions of NaOH and a quarternary ammonium salt. It is interesting to note that both the η^1 and η^3 products could be obtained and by varying the exact conditions of the experiment, yields and σ/π ratios of the products could be altered.

We sought to develop a phase-transfer reaction pathway to generate cyclopentadienyl-metal carbonyl anions which could then be made to react with a variety of organic species. It was hoped that this technique would provide routes to iron and ruthenium substituted allyl or alkyl derivatives. Our efforts in this regard will be described in the results and discussion section.

CHAPTER II

EXPERIMENTAL

All reactions were carried out under an atmosphere of prepurified nitrogen. Benzene and pentane were distilled over sodium prior to use. Tetrahydrofuran was distilled from sodium benzophenone under nitrogen. All other solvents were reagent grade and were used directly as obtained. Benzyltriethylammonium chloride (BTEAC), methyl iodide, crotyl bromide, allyl cyanide and allylamine were purchased from Aldrich Chemical Company and used directly. Allyl bromide (C_3H_5Br) was prepared using standard literature techniques.²⁴ The general work-up procedure for all phase-transfer reactions is outlined in the reaction description of $(\eta^5-C_5H_5)Fe(CO)_2Br$ with CH_3I , labelled reaction PT1.

Nuclear magnetic resonance spectra were obtained on a Varian FT-80A spectrometer with peak positions given in ppm downfield from tetramethylsilane (TMS). Infrared spectra were recorded on a Perkin-Elmer 257 instrument and calibrated against polystyrene film (1601.1 cm^{-1}). All spectral data are reported in Tables II-2 and II-3.

Conventional Preparation of a Variety of Cyclopentadienyl-Metal-Carbonyl Complexes

Preparation of $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ ²⁶

Iron pentacarbonyl, 18.75 ml (143 mmol), was added to 125 g of dicyclopentadiene in a 250-ml, three-neck flask fitted with a reflux condenser and a nitrogen inlet. Using an oil bath, the solution was maintained at a reflux temperature of 145°C for 24 hours while under nitrogen. After cooling slowly to room temperature, the deep purple solution was suction filtered. The purple crystals were washed with pentane and pumped to dryness yielding 25.5 g (50%) of product. Recrystallization was accomplished by dissolving the crude product in chloroform, filtering the solution and adding hexane to form crystals. The pure product was then collected by filtration and vacuum dried.

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$ ²⁷

3.5 g (9.9 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ was dissolved in a mixture of 50 ml CHCl_3 , 250 ml of 95% EtOH and 7.5 ml of concentrated HCl. After bubbling oxygen gas through the solution for three hours, the red solution was reduced to a residue by removal of the solvent at reduced pressure. The resulting residue was extracted into 300 ml of distilled H_2O and filtered. Extraction of the aqueous solution with 200 ml chloroform gave a deep red solution. After drying over anhydrous MgSO_4 , the solution was filtered. The filtrate was removed under reduced pressure to give a red solid. Crystallization from chloroform/petroleum ether gave 1.6 g (36%) yield of the desired product.

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ ²⁸

A solution of 0.44 ml (8.75 mmol) of bromine in 50 ml of CHCl_3 was added dropwise over one hour to a stirred solution of 2.72 g (7.7 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ in 150 ml of CHCl_3 at 0°C . The resulting solution was stirred for an additional two hours while maintained at 0°C . The dark red solution was washed with an aqueous solution of sodium thiosulfate (0.1M, 100 ml) and dried over anhydrous calcium chloride. After filtering, the solvent was removed by a rotary evaporator at reduced pressure. The addition of approximately 50 ml petroleum ether afforded a crude reddish-brown solid. Final purification was achieved by chromatography on a Grade III alumina/petroleum ether column. A red band was eluted with chloroform. Removal of the solvent gave 2.4 g (60%) of pure crystalline product.

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ ²⁹

2.0 g (7.9 mmol) of iodine was dissolved in 100 ml of chloroform. After addition of 2.0 g (5.7 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$, the solution was refluxed

under nitrogen for one hour. The black solution was cooled to room temperature and washed with an aqueous solution of sodium thiosulfate. The separated chloroform layer was dried over anhydrous MgSO_4 . Removal of solvent at reduced pressure gave a black solid. Sublimation at $90^\circ\text{C}/0.1\text{ mmHg}$ gave 2.5 g pure product (74%).

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$ ³⁰

2.5 ml (40 mmol) of CH_3I was added to the sodium salt, $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$, prepared via a Na/Hg/THF reduction of the dimeric species, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (4.4 g, 12.4 mmol). Filtration through celite removed the NaI by-product and gave a golden filtrate. After removal of the THF solvent, the product was purified by chromatography on Grade III alumina and eluted with petroleum ether/chloroform (10/1). Addition of pentane while cooling gave 3.4 g (55%) of pure golden needles of the product.

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_3\text{H}_5)$ ¹⁵

6.0 g (17 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ was reduced in 100 ml of THF using a 1-2% sodium amalgam. After stirring one hour at room temperature, the THF solution was extracted from the amalgam layer. While cooling the THF solution to 0°C , 3.55 ml (41 mmol) of allyl bromide in 50 ml THF was added dropwise over 45 minutes. The solution was allowed to warm to room temperature. Removal of the solvent under reduced pressure gave a brown oil. Due to the air-sensitivity of the material, no yield could be determined.

Preparation of $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ ²²

$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, 5.0 g (42.27% Ru) was dissolved in 50 ml of 95% formic acid and 38 ml concentrated hydrochloric acid. The solution was then refluxed for 2 days after which it was yellow in color. Removal of solvents, in vacuo,

afforded the crude product as a yellow paste which was used directly in the preparation of the cyclopentadienyl dimer described below.

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$ ²²

The ruthenium chlorocarbonyl dimer, $[\text{Ru}(\text{CO})_3\text{Cl}]_2$, was dissolved in 75 ml of freshly dried and distilled THF in a 250-ml three-neck flask. Sodium cyclopentadienide (2.7 g Na, 10 ml cyclopentadiene) was added dropwise over a two hour period. The resulting deep orange solution was refluxed overnight. The solution was cooled to room temperature and filtered under a nitrogen flush. Chromatographic purification on a Grade III alumina/petroleum ether column was possible using a 2/1 petroleum ether/dichloromethane mixture as the eluant. The solvents were removed to give an orange residue. Crystallization of product out of dichloromethane/pentane while cooled gave pure product (2.2 g, 48%).

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ ²²

An equimolar amount of bromine, 0.42 ml (8.1 mmol), dissolved in 200 ml of dichloromethane was added dropwise to a stirred solution of 3.6 g (8.1 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$ in 200 ml dichloromethane at 0°C. The resulting solution was stirred for an additional 30 minutes. The solvent was removed by a rotary evaporator at reduced pressure. The blackish-yellow residue was purified by column chromatography on florisil (60-100 mesh) with a 1/1 mixture of dichloromethane/hexane. An orange-yellow band was collected and the solvent removed under reduced pressure to give 3.8 g (78%) of pure yellow flaky product.

Phase-Transfer Catalysis Reactions

For all phase-transfer catalyzed preparations of Group VIII metal complexes described below, either one of two general procedures (Method A or B) was used.²⁴

Method A

Benzyltriethylammonium chloride (BTEAC) was dissolved in aqueous NaOH and added rapidly to a stirred solution containing reactants dissolved in dichloromethane or benzene. After the reaction was judged complete, the organic layer was separated and then dried over MgSO_4 . After filtering, the solvent was removed by a rotary evaporator at reduced pressure to afford the crude product. Purification procedures for the individual products are described within each section below.

Method B

A solution containing the metal carbonyl halide in dichloromethane or benzene was slowly added (drop addition) to a mechanically stirred mixture containing benzyltriethylammonium chloride (BTEAC) in aqueous NaOH and the organic halide to be complexed in a few ml of the organic solvent. After completion of the reaction, the organic layer was separated and then dried over MgSO_4 . After filtering, the solvent was removed by a rotary evaporator at reduced pressure to afford the crude product. Purification procedures for the individual products are described below.

Attempted Methyl Substitution using Method AReaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ with CH_3I under PTC Conditions (PT1)

0.23 g (1 mmol) of benzyltriethylammonium chloride (BTEAC) was dissolved in 20 ml of 5 N NaOH and added rapidly to a stirred solution containing 0.44 ml (6 mmol) of methyl iodide and 0.52 g (2 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ in 30 ml of benzene. The reaction was judged complete by the disappearance of the carbonyl bands of the starting material in the infrared spectrum. Following separation from the aqueous layer, the benzene component was dried over MgSO_4 and filtered. Reduction of volume and chromatography on alumina (Grade III) gave two bands. The first, a yellow one, eluted with petroleum ether. The second, red in color,

was eluted with a petroleum ether/chloroform solution (50/50). The yellow band was identified as the desired product, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$, while the red band was identified as the dimeric by-product, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ using infrared and nuclear magnetic resonance spectroscopy.

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ with CH_3I under PTC Conditions (PT2)

In a similar reaction to PT1, reaction PT2 was a three-fold increase of the previously described experimental conditions. This was done in an effort to aid in compound identification. All results agreed with those previously obtained.

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ with base in the presence of BTEAC (PT3)

0.23 g (1 mmol) of benzyltriethylammonium chloride was dissolved in 20 ml of 5 N NaOH and rapidly added to a stirred solution of 0.52 g (2 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ in 30 ml of benzene. The reaction was followed by infrared spectroscopy and judged complete by the disappearance of the stretching bands for the carbonyl groups of the iron starting material. After workup (outlined in PT1), the red product obtained was identified as the dimeric species, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$.

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ with base in the presence of BTEAC (PT4)

This reaction was a modification of that described in PT1, in that the concentration of the NaOH solution used was 1 N vice 5 N. The results obtained were consistent with those for PT1 in both product identity and yields.

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$ with base in the presence by BTEAC (PT5)

0.23 g (1 mmol) of benzyltriethylammonium chloride was dissolved in 20 ml of 5 N NaOH and rapidly added to a stirred solution of 0.39 g (2 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$ in 30 ml of benzene. The methyl starting material was inert under these conditions.

Attempted Allyl and Crotyl Substitutions

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ ($\text{X} = \text{Br}, \text{Cl}, \text{I}$) under Phase-transfer Conditions

(a) 0.23 g (1 mmol) of benzyltriethylammonium chloride (BTEAC) was dissolved in 20 ml of 5 N NaOH and added rapidly to a stirred solution containing 0.52 g (2 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ in 30 ml of benzene. The reaction was judged complete by the disappearance of the carbonyl bands in the infrared spectrum of the starting $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ complex. An aliquot was removed and dried over MgSO_4 . The infrared spectrum of the concentrated organic layer indicated a single product that was identified as $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$.

(b) In a similar reaction for the chloride derivative, the single product was identified as $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$.

(c) In a similar reaction for the iodide derivative, the single product was identified as $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$.

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ with Allyl Bromide under PTC Conditions

Typical Method A Reaction Quantities

In a typical reaction, 0.23 g (1 mmol) of benzyltriethylammonium chloride in 20 ml of 5 N NaOH was added to a solution containing 0.52 g (2 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ and 0.52 ml (6 mmol) of allyl bromide. After work-up, the reaction mixture was analyzed by nuclear magnetic resonance spectroscopy (Table II-2). The conditions of each preparative method are described in Table II-1.

Typical Method B Reaction Quantities

In a typical reaction, a solution containing 0.52 g (2 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ was added to a mixture containing 0.23 g (1 mmol) of benzyltriethylammonium chloride, 20 ml of 5 N NaOH, and 0.52 ml (6 mmol) of allyl bromide. After workup, the final organic layer was analyzed by Nuclear magnetic resonance spectroscopy (Table II-2) and the conditions are recorded in Table II-1.

Reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ with allyl cyanide and allylamine under PTC Conditions.

A variety of reactions, comparable to the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ with allyl bromide under PTC conditions, were conducted. In all cases, the only species identified in a measurable quantity was the dimeric species, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$. All attempts to synthesize allyl derivatives of the iron species from these organic reagents under PTC conditions were unsuccessful.

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ with base in the presence of BTEAC.

A solution containing 0.69 g (3 mmol) of benzyltriethylammonium chloride in 20 ml of 5 N NaOH was added rapidly to a mechanically stirred solution containing 0.3 g (1 mmol) of $\eta^5\text{-C}_5\text{H}_5\text{Ru}(\text{CO})_2\text{Br}$ in 30 ml of dichloromethane. Following workup, an infrared spectrum of the concentrated organic layer indicated that the ruthenium dimer, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$, was the only carbonyl-containing compound produced. The reaction was stopped at this point and discarded.

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ with allyl bromide under PTC conditions

A solution containing 0.69 g (3 mmol) of benzyltriethylammonium chloride in 20 ml of 5 N NaOH was added rapidly to a mechanically stirred solution containing 0.3 g (1 mmol) of $\eta^5\text{-C}_5\text{H}_5\text{Ru}(\text{CO})_2\text{Br}$ and 0.26 ml (3 mmol) of allyl bromide in 30 ml of dichloromethane. After the reaction was complete (15 min as evidenced by the disappearance in the infrared spectrum of the carbonyl bands of the ruthenium bromide complex), the dichloromethane layer was separated and worked up. The brownish-yellow residue was triturated with three 15 ml portions of hexane. The combined extracts were dried over MgSO_4 , filtered and the solvent was removed on a rotary evaporator to give a yellow solid which consisted of a 55:45 mixture of endo- and exo- $(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_3\text{H}_5)\text{Ru}(\text{CO})$ as determined by nuclear magnetic resonance spectroscopy (Table II-3).

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ with allyl cyanide under PTC conditions.

A solution containing 0.69 g (3 mmol) of benzyltriethylammonium chloride in 20 ml of 5 N NaOH was added rapidly to a mechanically stirred solution containing 0.3 g (1 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ in 30 ml of dichloromethane. After 45 min, the organic layer was worked up. A brownish-yellow residue was triturated with hexane to remove any allyl products from the reaction mixture. Cyclohexane extraction of the remaining original residue removed any dimeric species produced. All extracts were dried over MgSO_4 , filtered and reduced in volume to obtain nuclear magnetic resonance spectra.

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ with crotyl bromide under PTC conditions.

A solution containing 1.14 g (5 mmol) of benzyltriethylammonium chloride in 40 ml of 5 N NaOH was added rapidly to a mechanically stirred solution containing 0.50 g (1.7 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ and 0.52 ml (5 mmol) of crotyl bromide in 30 ml of dichloromethane. After the reaction was judged complete (45 min) by infrared spectroscopy, the dichloromethane layer was separated and worked up to yield a brownish-yellow residue. This residue was triturated with hexane. The hexane extract was dried over MgSO_4 , filtered and the solvent was removed under reduced pressure. The yellow paste was analyzed by nuclear magnetic resonance spectroscopy.

TABLE II-1 PTC Conditions for the Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ with Allyl Bromide

Rxn#	Iron Carbonyl Halide	$\text{CpFe}(\text{CO})_2\text{X}^c$ grams (mmol)	BTEAC grams (mmol)	Allyl Bromide ml (mmol)	Method	Time
1	$\text{CpFe}(\text{CO})_2\text{Cl}$	0.43(2)	0.23(1)	0.52(6)	A ^a	3 hrs
2	$\text{CpFe}(\text{CO})_2\text{Br}$	0.52(2)	0.23(1)	0.52(6)	A ^a	2 hrs
3	$\text{CpFe}(\text{CO})_2\text{Br}$	0.52(2)	1.38(6)	1.75(20)	B ^a	4 hrs
4	$\text{CpFe}(\text{CO})_2\text{Br}$	0.52(2)	2.3(10)	1.75(20)	B ^b	3 hrs
5	$\text{CpFe}(\text{CO})_2\text{Br}$	0.52(2)	2.3(10)	1.75(20)	B ^a	4 hrs
6	$\text{CpFe}(\text{CO})_2\text{I}$	0.61(2)	0.23(1)	0.52(6)	A ^a	54 hrs

a The organic solvent used was C_6H_6 .

b The organic solvent used was CH_2Cl_2 .

c $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$.

TABLE II-2 ^1H Nuclear Magnetic Resonance^a Data and Infrared Spectra^b in the CO Region.

COMPOUND	$\eta^5\text{-C}_5\text{H}_5$ (δ) ^a	ν CO (cm^{-1}) ^b
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$	4.77	1995, 1953, 1774
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}]$	5.06	2052, 2010 ^c
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}]$	5.04	2050, 2005
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}]$	5.04	2042, 2000
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3]$	4.60 ^e	2010, 1945
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_3\text{H}_5)]$	4.55 ^f	2010, 1948
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$	5.27	1972, 1964, 1942 ^d
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}]$	5.44	2050, 2000

^a Chemical shifts are relative to TMS in CDCl_3 unless otherwise noted.

^b Spectra recorded in CH_2Cl_2 unless otherwise noted.

^c Spectra recorded in CHCl_3 .

^d Spectra recorded in C_6H_{14} .

^e The CH_3 resonance is at 0.4 ppm relative to TMS.

^f Spectra recorded neat.

TABLE II-3 ^1H Nuclear Magnetic Resonance Data^a and Infrared Spectra in the CO Region
for $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\eta^3\text{-C}_3\text{H}_5)$.

$(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})(\eta^3\text{-C}_3\text{H}_5)$	$\eta^5\text{-C}_5\text{H}_5$	H	H_1, H_2 (J) ^d	H_3, H_4 (J) ^d	$\nu(\text{CO})$
			$\tau(\text{MR})(\delta)$		$\text{IR}(\text{cm}^{-1})$
1. <u>Endo-Ru</u> ^e	5.17s	4.08m	3.03d (6.3)	1.80d (11.0)	1937 ^b
2. <u>Exo-Ru</u> ^e	5.04s	4.07m	2.92dt (6.5)	1.28dt (10.6)	1958 ^b
3. $\pi\text{-Fe}(\text{exo})$ ^f	4.48s	4.33m	2.72dt (7.0)	0.47dt (11.0)	1962 ^c

^a Chemical shifts are relative to TMS, where s = singlet, d = doublet, dt = doublet of triplets and m = multiplet.

^b Spectra recorded in hexane.

^c Spectra recorded neat.

^d J coupling values are reported in () in Hz.

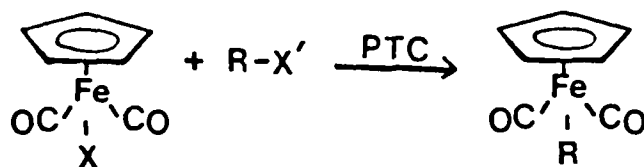
^e Spectra recorded in CDCl_3 .

^f Spectra recorded in CS_2 .

CHAPTER II

RESULTS AND DISCUSSION

Based on the observations of Gibson and coworkers²⁰⁻²⁴ concerning ligand substitution reactions which occur under phase-transfer conditions, it seemed viable that an OH^- catalyzed substituent replacement could take place with cyclopentadienyl metal carbonyl halides as illustrated in Scheme II-4.



where $\text{X} = \text{Br}, \text{Cl}, \text{I}$

Scheme II-4 General Phase-transfer Reaction

In the initial stages of this research, the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ with methyl iodide under phase-transfer conditions was investigated. It was found that the desired product, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_3)$, was generated under these conditions, but they were also found to give the dimer, $[\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$, as a significant by-product. In order to establish the sensitivity of the process to a variety of conditions and to optimize the product yields, a series of reactions were conducted. The conditions employed are summarized in Table II-4.

TABLE II-4 PTC Reactions^a of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ with methyl iodide, CH_3I

Rxn #	$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$	BTEAC	CH_3I	NaOH
	grams (mmol)	grams (mmol)	ml (mmol)	Norm.
PT1	0.52 (2)	0.23 (1)	0.44 (6)	5
PT2	1.56 (6)	0.69 (3)	1.32 (18)	5
PT3	0.52 (2)	0.23 (1)	0.00 (0)	5
PT4	0.52 (2)	0.23 (1)	0.44 (6)	1

^a All reactions were conducted at room temperature in benzene.

By monitoring the reactions using infrared spectroscopy, the production of the methyl species and the consumption of the bromide starting material could be followed. Samples were removed at various time intervals, the solvent removed and the residue dissolved in dichloromethane. After drying with MgSO_4 , infrared spectra of these solutions were easily obtained.

The reaction identified as PT1 was the first attempt to generate the intended product. After completion of the reaction as determined by infrared spectroscopy, the products were dried and chromatographed on a Grade III alumina column. Two complexes were isolated which were shown to be $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_3)$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ by infrared and nuclear magnetic resonance spectroscopy. A second run (PT2) was conducted on a larger scale and gave identical results. This experiment indicated a four-fold decrease in reaction time as compared to the conventional synthesis of this methyl compound.

In an attempt to understand the formation of large quantities of the dimer along with the desired methyl compound, reaction PT3 was run without the methyl iodide reactant. It was found that $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ rapidly disappears from the reaction mixture with the formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ as the sole product. The reaction is essentially complete within minutes and the dimer is isolated in high yield.

An additional concern besides the stability of the starting material under phase-transfer conditions was the effect that the concentration of the aqueous base solution would have on the generation of product (PT4). Reduction of the strength of the base from 5 N NaOH to 1 N NaOH has no apparent effect on the product selectivity, yield or reaction time.

In order to expand the scope of this study, additional experiments were investigated in which allylic reagents were added to cyclopentadienyl metal carbonyl halide complexes under phase-transfer conditions. As a second feature of this portion of the work, the metal identity was expanded to include ruthenium.

The reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ (where $\text{X} = \text{Br}, \text{Cl}, \text{I}$) with base under phase-transfer conditions readily led to the formation of the dimeric species, as indicated above. This can be attributed to the high nucleophilicity of the of the anion species $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ generated, which in turn acts to displace the halide from molecules of the starting material. The relative reactivities of the iron halide starting materials, under phase-transfer conditions, were made by comparison of the rate of dimer formation as judged by infrared spectroscopy. The iodide complex was found to be the least reactive. The chloride and bromide complexes showed comparable reaction rates with the overall order being $\text{Cl} > \text{Br} \gg \text{I}$. The electronegativity of the halides themselves decrease in the same order. It was expected that the increase in electron donation to the metal would result in a decreased reactivity, as was observed.

From additional observations, the effectiveness of the phase-transfer system also appeared to be dependent upon several other factors.² These included 1) the identity of the quaternary salt, 2) the polarity of the organic solvent and 3) the identity of the organic reagent.

IDENTITY OF THE QUARTENARY SALT CATALYST

Quaternary salts of the type $\text{RN}^+(\text{R}')_3\text{X}$, where R and R' are carbon chains, are frequently used as catalysts due to the ease of preparation and/or commercial

availability. Generally, the trimethyl salts are avoided because of a strong tendency to complicate the reaction by forming stable emulsions. Catalysts where R' are longer carbon chains appear to activate the transfer of anionic species between the aqueous and organic phases. In addition, more symmetrical cations are better than those having one long carbon chain.

The reaction rate is proportional to the amount of the quaternary salt present because the concentration of this salt determines the amount of reactants in the nonaqueous phase. The ability of the ion to transfer between phases is partially determined by the identity of the counterion of the salt. The extent of anion hydration slows the transfer process even though the water of hydration may or may not accompany the anion to the organic phase. A second consideration is the interaction of the quaternary cation with its counterion. Highly lipophilic anions such as I^- strongly bind to the quaternary cation and inhibit ion exchange.

POLARITY OF THE ORGANIC SOLVENT

The amount of quaternary ammonium hydroxide present in the organic phase is dependent upon both the organic solvent used and the concentration of the aqueous base. With concentrated base solutions (5N) and benzene as the organic phase, less than 2% of the quaternary compound is present in the organic phase. The use of this solvent often results in an oily suspension of quaternary compound between the organic phase and the aqueous phase. In similar reactions conducted with the more polar solvent such as dichloromethane, more than 97% of the quaternary salt is found in the organic phase and no emulsion is formed.

IDENTITY OF THE ORGANIC REAGENTS

As previously indicated, the iron dimer is generated in significant concentration through a reaction which competes with the synthesis of the desired alkyl compound. It appears that the $[(n^5-C_5H_5)Fe(CO)_2]^-$ species which is formed under phase-transfer conditions reacts competitively with $(n^5-C_5H_5)Fe(CO)_2Br$ and CH_3I .

Even at relative ratios of 3/1 of CH_3I to the bromide starting material, the reaction to form the dimer predominates. The failure of the methyl iodide to react at a significant rate with the organometallic intermediate remains a puzzle. Of particular interest is the observation that if the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ is the reactive intermediate, it appears to react preferentially with the least likely reagent from a steric consideration. While the iron and carbon centers of the reagents are formally tetrahedral, the cyclopentadienyl ring in the iron moiety effectively shields the iron atom from attack. Furthermore, it is known that the same anionic species generated by the conventional method of sodium amalgam reduction, reacts well with methyl iodide. In an effort to gain insight into the sensitivity of the reaction to the organic reagent and perhaps also to the identity of the intermediate, the investigation was expanded to include allyl derivatives.

The initial studies of the formation of allyl iron complexes via phase-transfer conditions were reported by D.H. Gibson and W.-L. Hsu in 1980.²⁰⁻²⁴ These studies, described in detail, indicated relative yields of σ/π allyl complexes and the dimer by-product under a variety of conditions. To develop a familiarity with these procedures, several of the reactions of allyl bromide with $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ where $\text{X} = \text{Br}, \text{Cl}, \text{I}$ were duplicated in this research. Table II-1 summarizes selected reaction conditions used. The reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ with a three-fold excess of allyl bromide introduced by rapid addition were found to give comparable results to those reported by Gibson and Hsu. The relative yields of dimer formed increased in the order $\text{I} < \text{Br} < \text{Cl}$. The ratios of σ/π allyl species were relatively insensitive to the identity of the starting organometallic halide. In all cases, slightly more of the σ -allyl species was obtained than the π complex.

It was found that the rate of addition affected the product yields from the reaction. Two addition methods were employed in these studies. One involved

dropwise addition of the iron halide in the organic solvent to the phase-transfer catalysis media consisting of the catalyst, the aqueous base solution and the allyl bromide. The alternative approach was to rapidly add a solution of the catalyst in the hydroxide base to the organic solvent containing the organo-metallic halide complex and the allyl bromide. Again, in agreement with the results of Gibson and Hsu, it was found that rapid addition resulted in a mixture which was predominately the σ complex and the dimer by-product. Slow addition gave primarily the π complex. These observations held even though the reactants were together over the same period of time since the rapid addition reaction mixture was subsequently stirred for several hours after initial mixing. This suggests that the σ complex formed upon rapid addition is either not being converted into the π complex or the reaction is very slow under phase-transfer conditions. This further implies that upon slow addition, the π complex must be immediately formed. This latter observation is difficult to reconcile in terms of an anionic reactive intermediate, as was previously suggested. This appears to be inconsistent with the conventional preparative route for the methyl complex, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_3)$, formed from $\text{Na}^+ [(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ with CH_3I . Formation of this methyl complex under PTC methods appears to require the generation of the same anionic intermediate. However, if this species is being generated under slow addition conditions, then the σ -allyl complex would be expected as the major product. Since the σ species is not converted to the π complex under phase-transfer conditions, an alternate mechanism must be required to explain the formation of the π complex.

In the reactions described above, the solvent was the nonpolar compound benzene. Since the proposed anionic intermediate would be stabilized in a polar solvent, a series of reactions were run in dichloromethane. If this solvent were in fact stabilizing the anionic species, it was felt that the relative concentration of the σ complex would be increased. This trend was found to be true

for both the rapid and slow addition methods. These results further support the idea that two competitive mechanisms are responsible for the generation of the σ and π products. The exact nature of the mechanism required for the π complex is not clear although an electron deficient species may be implicated.

To clarify an additional aspect of these reactions, a series of allyl derivatives, C_3H_5X , were used as the organic reagents. In these derivatives, the X group was either Br, CN or NH_2 . These groups differ in their ability to leave the carbon of the allyl upon attack by a nucleophile. The experimental results which were obtained indicate that the cyano and amine could not be removed from the allyl moiety under a variety of phase-transfer conditions. As a result, in those reactions using these two reagents, only the dimeric species, $[(\eta^5-C_5H_5)Fe(CO)_2]_2$, was generated.

It is common knowledge that the heavier members of a metal triad (eg., Fe, Ru, Os) are better able to stabilize electron-deficient species. As a result, it was determined that another aspect which might be considered was the identity of the metal in the organometallic halide species. These comparative studies have thus far been limited to an examination of the reaction of $(\eta^5-C_5H_5)Ru(CO)_2Br$ with allyl bromide and allyl cyanide under phase-transfer conditions. It has been found that unlike the iron system, both allyl compounds react to give products. The allyl bromide gives exclusively the π complex, while the allyl cyanide give both the π complex and the ruthenium dimer, $[(\eta^5-C_5H_5)Ru(CO)_2]_2$. It should be noted that under no conditions was any of the σ complex observed.

In contrast to the iron π -allyl system, endo/exo isomers (Figure II-1) can be observed by nuclear magnetic resonance spectroscopy. Relative integrations of the cyclopentadienyl resonances indicate that these isomers are present in approximately equal concentrations. In the iron case the allyl group is found to exist only in the exo conformation.

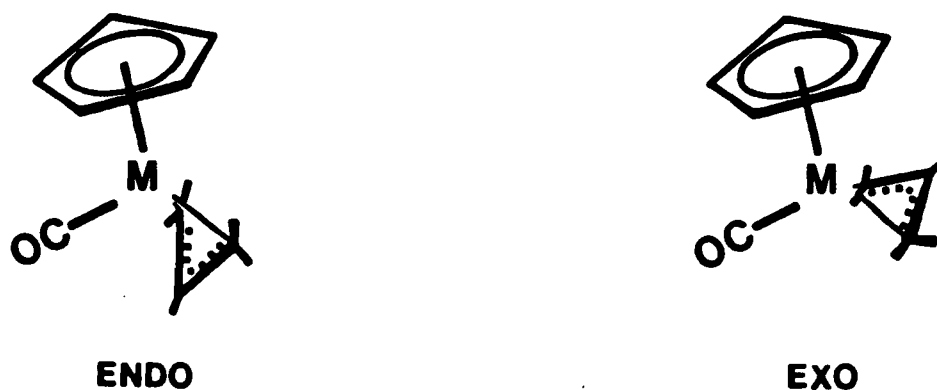


Figure II-1 Possible Endo/Exo Conformations

In a preliminary effort to determine the reactivity of the ruthenium halide complex with substituted allyl bromide, the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ with crotyl bromide was examined. It was predicted that the crotyl ligand could adopt four isomeric conformations. The endo/exo isomers, previously described, can themselves each exhibit two arrangements, designated syn and anti (Figure II-2). While it was not possible to separate the ruthenium-crotyl complexes from the reaction mixture, NMR spectra indicate the presence of four distinct cyclopentadienyl ring resonances which may correspond to these four stereoisomers. Considerable additional work on the crotyl system and other substituted allyl derivatives seems warranted.

The experimental results which have been described above lay the ground work for much additional study into the application of phase-transfer catalysis to organometallic synthesis. Specific questions which remain to be resolved are the identities of the reactive intermediates in both the iron and ruthenium systems, the effect of solvent polarity on the specificity of product formation, the role of water in these reactions and the possibility of producing a range of additional substituted-allyl metal derivatives.

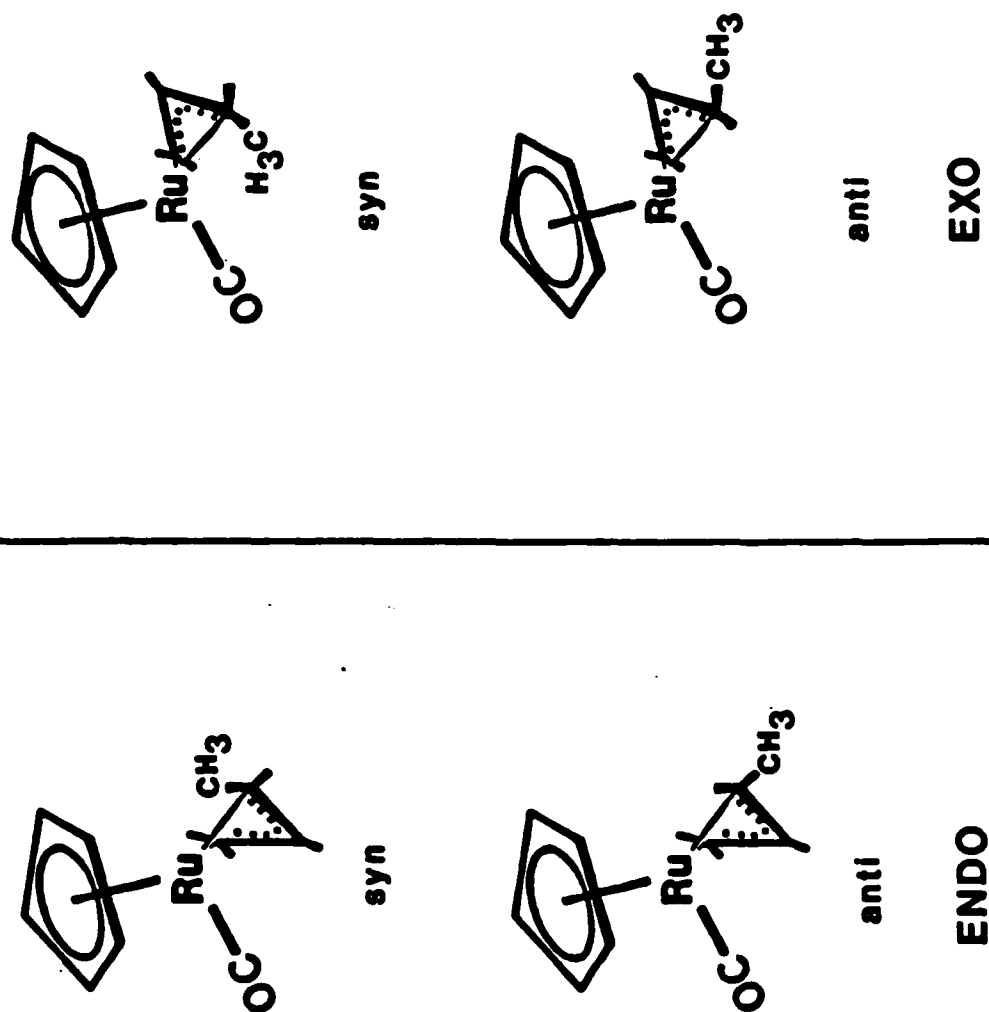


Figure II-2 Stereoisomeric Conformations for the Crotyl Derivative

CHAPTER II

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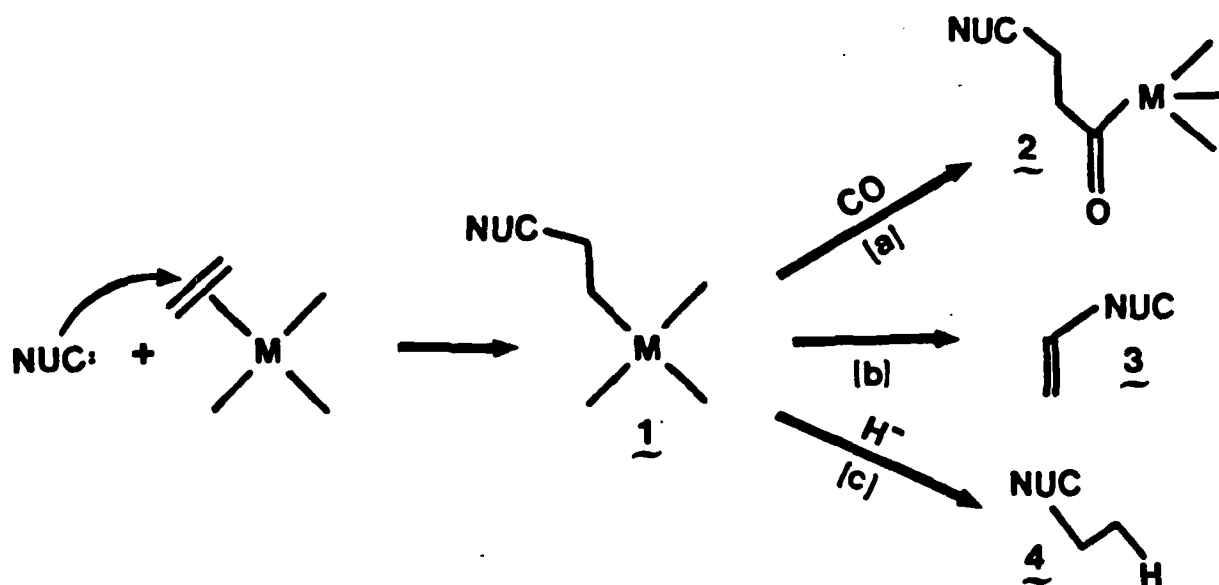
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CHAPTER III

SYNTHESIS OF METAL COMPLEXES USING PHOTOLYSIS

INTRODUCTION

A number of metal olefin complexes, particularly those of Pd(II), Pt(II) and $[\text{Fe(II)}]^+$ undergo attack by electron-donating molecules,¹ referred to as nucleophiles. Complexation of such heteroatomic species as amines (NH_3), phosphines (PR_3) or methanol (CH_3OH) results in the formation of σ -alkylmetal complexes (Scheme III-1, 1). If stable, further reaction of these initial products can result in organometallic derivatives being formed. An example of one of the many types of reactions possible is a carbonylation process in which a CO molecule is inserted into the metal-alkyl linkages (Scheme III-1, pathway a, 2). Often, these σ -alkyl groups can be removed from the metal by either spontaneous β -hydride elimination (Scheme III-1, pathway b, 3) or hydride attack at the metal-bound carbon (Scheme III-1, pathway c, 4).



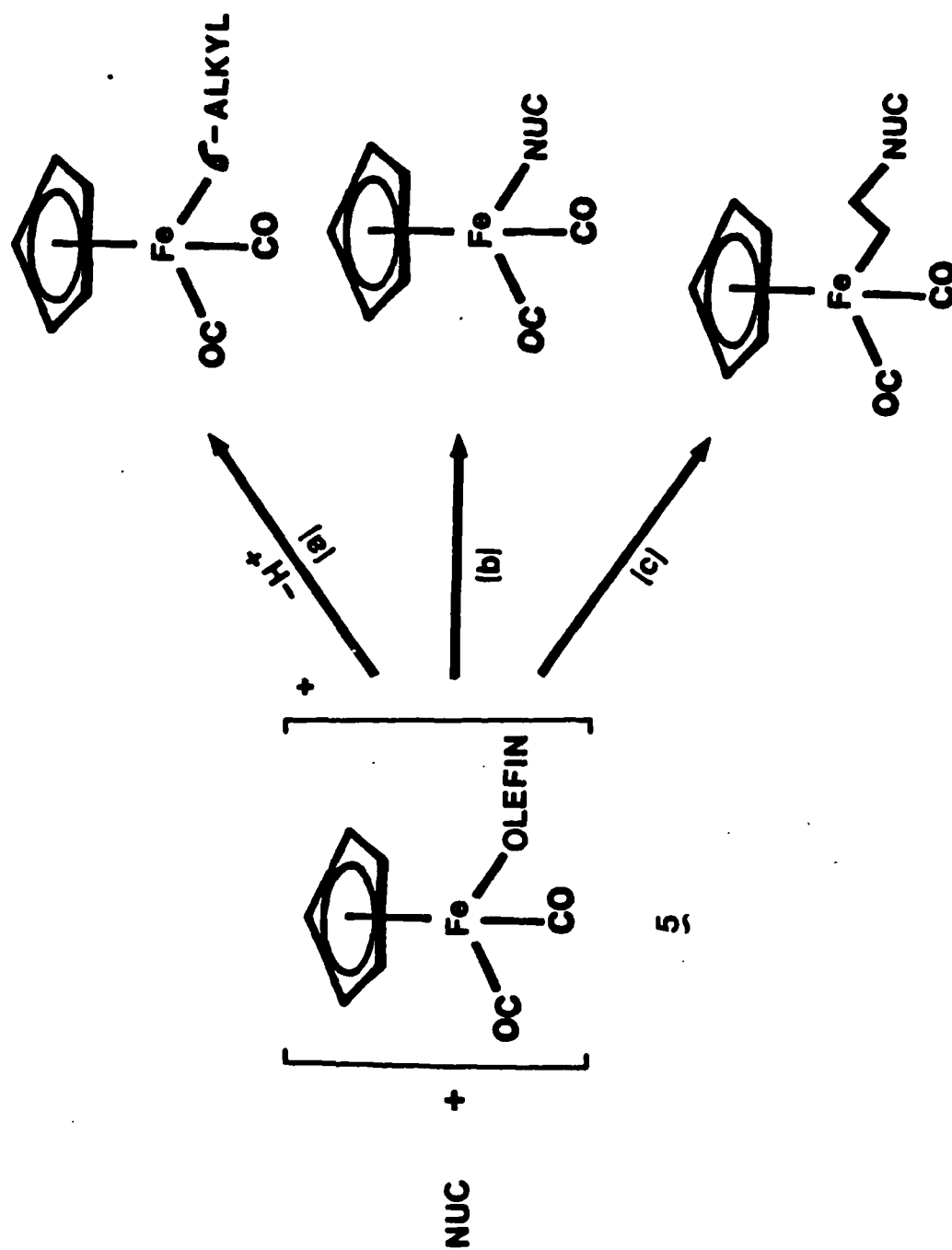
Scheme III-1 Possible Reaction Pathways for Metal-Nucleophilic Species

The inherent ability of metal-complexed olefins to act as electron acceptors with respect to a wide range of nucleophilic species was explored in great depth during the 1970's.²⁻⁴ A general observation has been the strong electron-donating ability of the olefin ligand to the metal center, resulting in a slightly unbalanced electron charge transfer to the metal. As a result, the olefin ligand assumes a slightly positive character and will undergo metal-assisted nucleophilic addition to form a variety of transition metal complexes.

The development of the chemistry of the cationic $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{olefin})]^+$ complexes (Scheme III-2, 5) is primarily due to the research efforts of M. Rosenblum and co-workers.⁵⁻⁷ These workers have demonstrated that $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{olefin})]^+$ complexes react with an extensive array of nucleophiles to produce stable, neutral σ -alkyl iron complexes. Several reaction pathways are possible, as illustrated in Scheme III-2. The actual reaction pathway followed, such as allylic deprotonation (pathway a), olefin displacement (pathway b) or addition reaction (pathway c) was found to be dependent upon both the identities of the nucleophile and the olefin. Addition of both carbon and heteroatomic nucleophiles occurs primarily, or exclusively, at the most substituted olefinic position.^{1,8-12} In the absence of excessive steric demands, the formation of the stereospecific trans isomer results. Addition reactions to monosubstituted olefin complexes are not very regiospecific* for simple alkyl substituted alkenes. The degree of regiospecificity, however, can be greatly enhanced by the presence of electron-withdrawing substituents such as CHO, C(O)R, or CO₂R on the olefin. In this way, one can selectively prepare regiospecific products under mild reaction conditions and in high yield.

While the cationic $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{olefin})^+$ complexes and their reaction

* regiospecific¹³: "A reaction is described as regioselective if an unsymmetrical olefin gives a predominance of one of the possible addition products; the term regiospecific is used if only one possible product is formed."



Scheme III-2 Reaction Pathways for Nucleophilic Additions

with nucleophilic reagents have been extensively studied, an in-depth analysis of the ethylene derivative was not reported until 1975.¹⁴ Reaction of the anionic complex $\text{Na}^+ [(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ with a tetrahydrofuran solution of ethyl halide, $\text{C}_2\text{H}_5\text{X}$, at -78°C gave the ethyl derivative, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_5)$. Subsequent hydride abstraction with trityl tetrafluoroborate, $(\text{O}_3\text{C})^+\text{BF}_4^-$, gave the desired cationic species, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)]^+ \text{BF}_4^-$. Temperature-dependent nuclear magnetic resonance (NMR) studies revealed that the olefinic ligand could exist in two possible orientations relative to the metal center (Figure III-2).

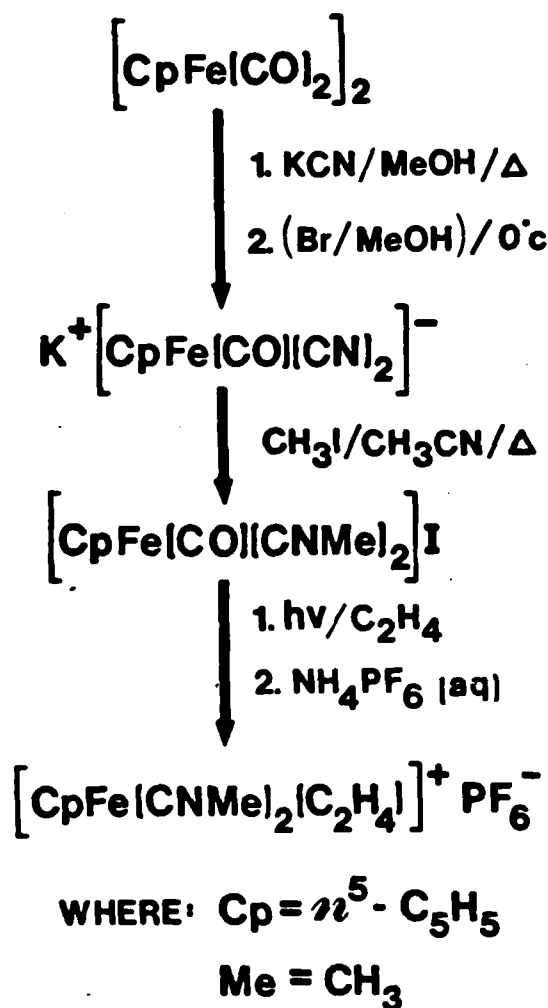


Figure III-2¹⁴ Possible Orientations of Ethylene in $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)]^+ \text{BF}_4^-$

At room temperature, the ethylene rotates rapidly about the metal-olefin bond, which averages the magnetic environment of the olefin. This "averaging" process can be detected in the NMR spectrum by the presence of a simple singlet for the ethylene protons. By subsequently lowering the temperature to approximately -80°C , a signal broadening is observed, indicative of hindered rotation about the iron-ethylene bond. By comparison of this system with an indenyl derivative, $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)]\text{BF}_4$, and an analysis of the variations of chemical shifts of the protons, it was determined that the preferred orientation of the ethylene ligand is one in which the $\text{C}=\text{C}$ bond is parallel to the plane of the

cyclopentadienyl ring (7). This arrangement minimizes the steric interactions of the complex and thus makes it thermodynamically favored.

A. L. Steinmetz and B. V. Johnson¹⁴ have recently reported the synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CNCH}_3)_2(\text{C}_2\text{H}_4)]^+\text{PF}_6^-$ which is directly analogous to the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)]^+\text{BF}_4^-$ complexes described above. In this complex, CO is replaced by CNCH_3 which is electronically similar in both its electron donating and back-bonding capabilities. The synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CNCH}_3)_2(\text{C}_2\text{H}_4)]^+\text{PF}_6^-$ is shown in Scheme III-3.



Scheme III-3 Synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CNCH}_3)_2(\text{C}_2\text{H}_4)]^+\text{PF}_6^-$

The strong similarity of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CNCH}_3)_2(\text{C}_2\text{H}_4)]^+ \text{PF}_6^-$ to the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)]^+ \text{BF}_4^-$ compound suggests that these new isocyanide materials may be capable of participating in the same extensive variety of nucleophilic reactions as their carbonyl analogues. In an effort to examine this possibility, exploratory studies were conducted directed toward the synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CNCH}_3)_2(\text{C}_2\text{H}_4)]^+ \text{PF}_6^-$ and its ruthenium analogue. It was intended that the reactions of these compounds with nucleophiles would be studied. The results of these studies will be described below.

CHAPTER III

EXPERIMENTAL

All reactions were carried out under an atmosphere of prepurified nitrogen. Solvents were of reagent grade quality and were used as obtained, with the exception of methanol which was dried over magnesium and iodide and then distilled prior to use. Photochemical reactions of the ruthenium complexes utilized a 450-watt Ace-Hanovia Photochemical Unit. During photolytic reactions, the solutions were purged with a steady flow of nitrogen. Chromatographic separations utilized neutral alumina (FISHER A-540).

Nuclear magnetic resonance spectra were obtained using a Varian FT-80A spectrometer with reported peak positions given in ppm downfield from tetramethylsilane (TMS). Infrared spectra were recorded in the carbonyl region ($2500 - 1600 \text{ cm}^{-1}$) on a Perkin-Elmer 257 spectrophotometer and calibrated against polystyrene film (1601.1 cm^{-1}). All spectral data are reported in Tables III-1 and III-2.

Preparation of $\text{K}^+ [(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CN})_2]^-$ ¹⁶

In a typical reaction, 14.2 g (40 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ¹⁷ is combined with 20.8 g (320 mmol) KCN in 300 ml of dry methanol. The purple reaction mixture was refluxed for thirty minutes under an atmosphere of prepurified nitrogen. Following the removal of heat, the orange solution was allowed to cool to room temperature while stirring. After cooling further to 0°C , 58 ml of a bromine/methanol (9.1 ml/190 ml) solution was added dropwise. The resultant solution was filtered through celite and the filtrate rotovapped to dryness. The residue obtained was dissolved in minimal hot ethanol and again filtered through celite. Cold ethyl ether (0°C) was added to the filtrate to give golden crystals of the desired product, which were collected by filtration and pulled to dryness on a vacuum pump. (11.8 g, 61.4%)

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNCH}_3)_2]^+ \text{PF}_6^-$ ¹⁶

A solution of 1.2 g (5 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CN})_2]$ and 0.75 ml (12 mmol) of CH_3I in 150 ml acetonitrile was refluxed under nitrogen for 72 hours. After cooling, the solution was rotovapped to dryness. The resulting residue was purified by chromatographic separation on a neutral alumina column. Elution with dichloromethane followed by a dichloromethane/methanol solution (4/1) afforded a golden band. Removal of the solvent and addition of petroleum ether gave a yellow powder, the desired product. Recrystallization from chloroform/hexane gave yellow crystals (0.85, 60%). By addition of a saturated solution of NH_4PF_6 , the iodide counterion of the initial product was exchanged with a PF_6^- counterion to result in the final product.

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CNCH}_3)_2(\text{C}_2\text{H}_4)]^+ \text{PF}_6^-$ ¹⁵

While being irradiated for approximately one hour, ethylene gas was bubbled through a solution of 0.5 g (1.4 mmol) $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNCH}_3)_2]\text{PF}_6^-$ in 150 ml of dichloromethane. The solution was concentrated and the infrared spectrum taken of the reaction mixture. None of the desired product was obtained.

Preparation of $\text{K}^+ [(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CN})_2]^-$ ¹⁸

$(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ ¹⁹ (3.17 g, 10.5 mmol) and 3.17 g (48.7 mmol) KCN were combined in 175 ml of dry methanol and refluxed under nitrogen for 16 hours. The solvent was removed under reduced pressure leaving a brownish solid. After four extractions (4 x 25 ml) with acetonitrile, the resulting amber solution was filtered and concentrated until crystallization began (~ 20 ml). Approximately 70 ml diethyl ether was added to precipitate the product as grey flakes, which were collected by filtration and air dried (0.82 g, 27%).

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CNCH}_3)_2]^+ \text{I}^-$ 18

$\text{K}^+ [(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CN})_2]^-$ (0.75 g, 2.6 mmol) was dissolved in 100 ml acetonitrile. Following the addition of 3.75 ml CH_3I (59 mmol) the solution was refluxed for 16 hours. Removal of solvents under reduced pressure left a pale beige residue which was redissolved in 20 ml of chloroform and filtered. After the volume had been reduced to 10 ml, minimal ethyl ether was added to precipitate a grey product which was the iodide salt. After collecting the product by filtration, it was air-dried to yield 0.87 g (82%).

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CNCH}_3)_2]^+ \text{PF}_6^-$ 18

A 10 ml aqueous solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CNCH}_3)_2]^+ \text{I}^-$ (0.60 g, 1.5 mmol) was added to a saturated aqueous solution of NH_4PF_6 . An anion-cation exchange occurred, yielding the product $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CNCH}_3)_2]^+ \text{PF}_6^-$ which precipitated out of solution with cooling. The product was collected and dried to yield 0.57g of beige crystals (90%).

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CNCH}_3)_2\text{I}]$

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CNCH}_3)_2]^+ \text{I}^-$ (0.25g, 0.63 mmol) was dissolved in approximately 250 ml of dichloromethane and irradiated for 80 minutes while under a constant flow of nitrogen. The resulting green solution was concentrated to approximately 5 ml and chromatographed on a column of neutral alumina prepared with petroleum ether. The desired product was eluted as an orange band with 3% methanol in dichloromethane. Removal of all solvents yielded the product as an orange oil.

Attempted Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CNCH}_3)_2(\text{C}_2\text{H}_4)]^+ \text{PF}_6^-$ 19

Ethylene was bubbled through a solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CNCH}_3)_2]^+ \text{PF}_6^-$ (0.50 g, 1.2 mmol) in approximately 250 ml of dichloromethane and irradiated for

90 minutes. The solution was concentrated to 5 ml and chromatographed on a neutral alumina column prepared with petroleum ether. None of the desired product was isolated.

TABLE III - 1 Infrared Spectra in the CO and CN Stretching Regions (2500 - 1600 cm^{-1})^a

COMPOUND	$\nu \text{ CO } (\text{cm}^{-1})$	$\nu \text{ CN } (\text{cm}^{-1})$	$\nu \text{ CNCH}_3 (\text{cm}^{-1})$
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2^b$	1995, 1953, 1774		
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CN})_2]^-^d$	1950	2085	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNCH}_3)_2]^+^c$	2024		2228, 2207
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2^c$	1972, 1964, 1942		
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}]^b$	2050, 2000		
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CN})_2]^-$	1953	2106, 2095	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CNCH}_3)_2]^+^c$	2026		2238, 2211
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CNCH}_3)_2]\text{I}]$			2173, 2135

^a Spectra recorded in CHCl_3 unless otherwise noted.^b Spectra recorded in CH_2Cl_2 .^c Spectra recorded in C_6H_{14} .^d Spectra recorded in CH_3CN .

TABLE III-2 ^1H Nuclear Magnetic Resonance Data ^a

<u>COMPOUND</u>	<u>$\eta^5\text{-C}_5\text{H}_5$</u>	<u>CNCH_3</u>
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$	4.77	-
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CNCH}_3)_2]^+ \text{ }^b$	5.33	3.64
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$	5.27	-
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}]$	5.44	-
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CN})_2]^- \text{ }^c$	5.10	-
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CNCH}_3)_2]^+ \text{ }^b$	5.68	3.67
$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CNCH}_3)_2\text{I}]^b$	4.35	3.58

^a Chemical shifts are relative to TMS in CDCl_3 unless otherwise noted.

^b Spectra recorded in acetone - d_6 .

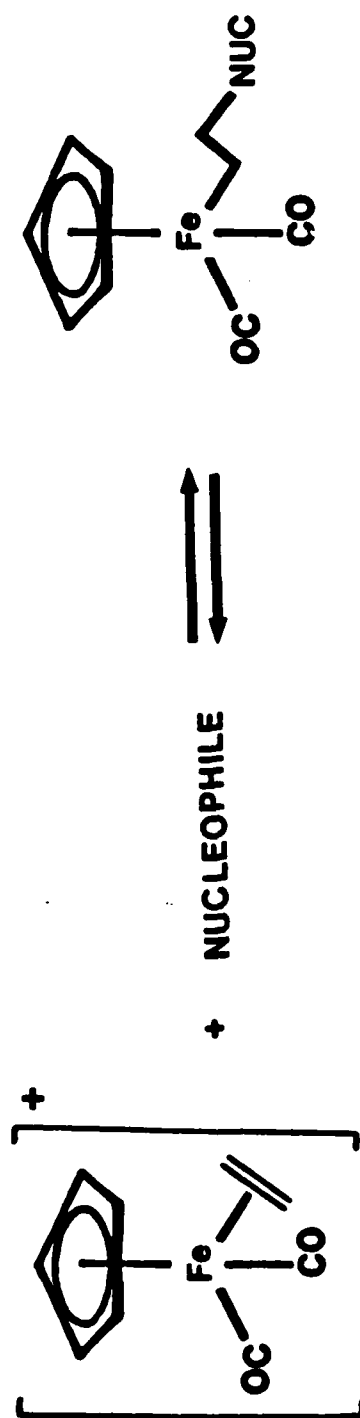
^c Spectra recorded in CD_3CN .

CHAPTER III

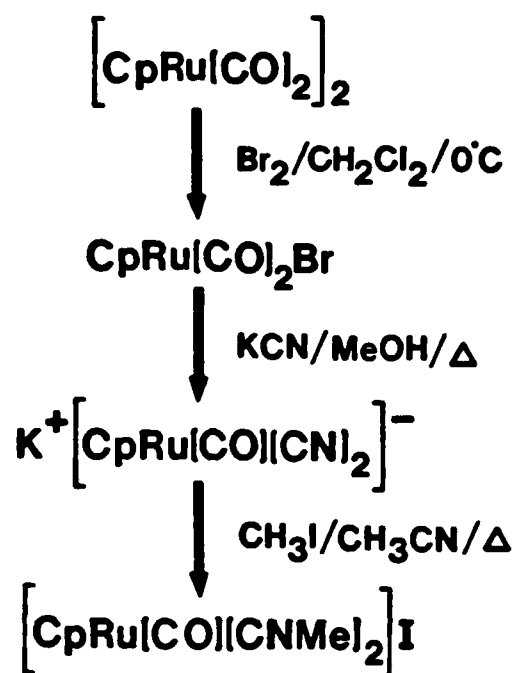
RESULTS AND DISCUSSION

Rosenblum⁷ has developed the chemistry of cationic $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{olefin})]^+$ complexes, which undergo attack at the olefin by a wide range of nucleophiles to produce stable, neutral σ -alkyliron complexes (Scheme III-4). This cationic olefin complex was determined to be more susceptible than neutral complexes to attack by nucleophiles. The major contributing factor for such a reaction is the ability of the olefin to accommodate the pair of electrons it gains as a result of the nucleophilic attack. It seemed viable that similar results might be obtained for the isocyanide derivative, $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CNCH}_3)_2(\text{olefin})]^+$ where M = Fe or Ru.

A series of reactions were first necessary to generate a $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})-(\text{CNCH}_3)_2]^+ \text{I}^-$ salt. As outlined in Scheme III-5, the methylated iodide salt of ruthenium was obtained through a multistep process. Dropwise addition of bromine in chloroform at 0°C to a solution of cyclopentadienyl-ruthenium-carbonyl dimer in chloroform yielded the monomeric species, $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$. Subsequent reaction of this material with KCN in methanol at reflux temperatures gave grey flakes of $\text{K}^+[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{CN})_2]^-$. Methylation with two equivalents of methyl iodide in acetonitrile with refluxing provided the bis-methyl derivative directly. Purification from an ethyl ether/chloroform solution gave a grey crystalline material which was collected by filtration. A similar synthetic pathway to produce the analogous iron bisisocyanide complex was described in the introduction in Scheme III-3.



Scheme III-4 Nucleophilic Attack on Iron Olefin Complexes

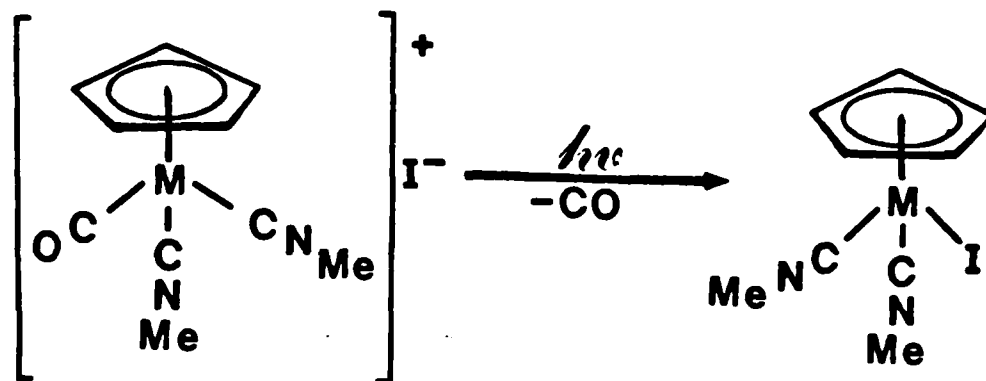


WHERE: $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$
 $\text{Me} = \text{CH}_3$

Scheme III-5 Synthesis of a Bisocyanide Ruthenium Salt

It is known that the ethylene product $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{CNCH}_3)_2(\text{C}_2\text{H}_4)]^+ \text{PF}_6^-$ can be obtained through the photolysis of the bisisocyanide derivative (1) in the presence of the olefin. The primary photochemical path (Scheme III-6) for the preparation of these metal olefin complexes involves the formation of an electron-deficient species (2) by the removal of a carbonyl ligand from the metal center. The ethylene product (3) is formed by simple complexation of the free ethylene being bubbled through the solution.

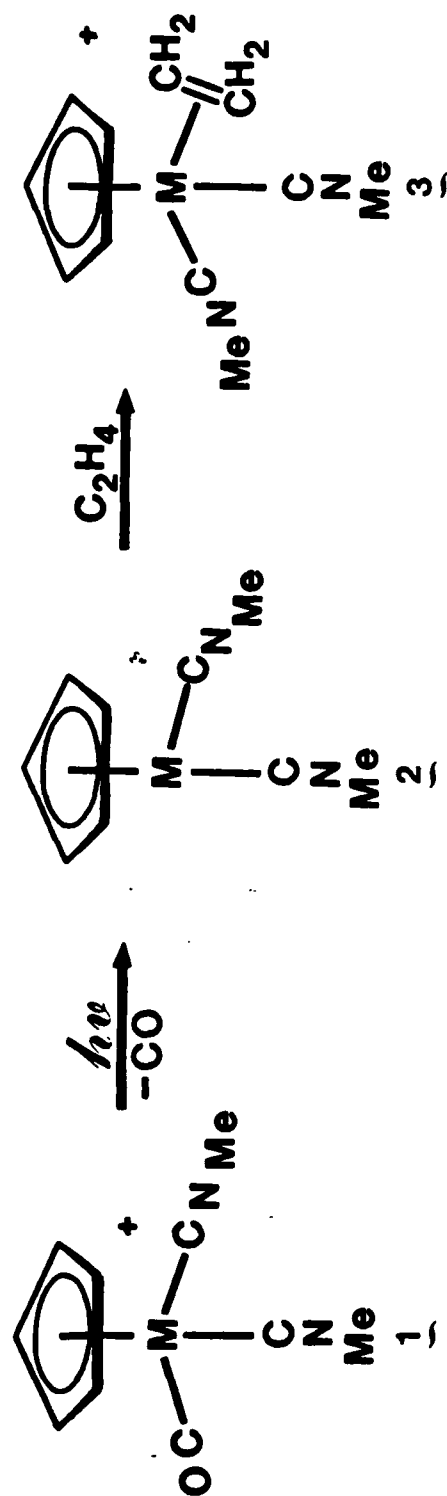
Preliminary irradiation reactions revealed that under photochemical conditions, the iodide counterion of the bisisocyanide salt complex undergoes substitution as seen in Scheme III-7. The exchange of the iodide counterion for a larger,



Scheme III-7 Production of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{CNCH}_3)_2\text{I}]$

inert PF_6^- counterion was expected to prevent such side reactions from taking place. This exchange was accomplished through the addition of the metal-bisisocyanide salt to an aqueous solution of NH_4PF_6 . The subsequent photochemical reaction of the species $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{CNCH}_3)_2(\text{CO})]^+ \text{PF}_6^-$ in the presence of ethylene was then attempted. Unfortunately, the desired product was not obtained.

It appears that the desired ethylene product was being photochemically decomposed by the high energy ultraviolet radiation generated by the light source



Scheme III-6 Generation of $[(\eta^5-C_5H_5)M(CNCH_3)_2(C_2H_4)]^+$

used in the experiment. This problem can be relieved or eliminated in the future through the use of a Vycor sleeve in the photochemical cell. This would effectively filter out uv radiation from the lamp and would prevent such radiation from reaching the sample solution. As a result, lower energy radiation would reach the sample and might be of the appropriate energy to effect the desired substitution. If it is possible to correct the synthesis of the ethylene species by this simple technique, then it should be possible to produce moderate quantities of the desired ethylene complex. With this material in hand, the studies on the nucleophilic reactions could be easily pursued.

CHAPTER III

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CHAPTER IV

CONCLUSION

Organometallic chemistry had its origins in the study of metal-catalyzed reactions directed toward the synthesis of useful organic compounds. Although the studies began with investigations of reactions catalyzed by bulk metals, it quickly became apparent that highly-selective reactions could be mediated by organometallic complexes containing a single metal center. Research has indicated that the speed and selectivity of these processes are dependent on several subtle factors, including the nature, size and shape of the ligands and the identity of the metal center.

Considerable research has been reported describing the uses of cyclopentadienyl-iron dicarbonyl complexes to the catalysis of organic reactions. Convenient and rapid synthetic routes for the preparation of the organometallic compounds are prerequisites for their broad application and economical use. The research described in this paper has primarily been directed towards the extension of phase-transfer catalytic techniques to the preparation of iron and ruthenium allyl complexes. These species are potentially valuable precursors for extending the chemistry of cyclopentadienyl-metal-carbonyl systems.

Phase-transfer catalysis involves the application of large quaternary ammonium cations to transport reactive anions, such as hydroxide, between an aqueous and an organic phase. It has been found that when hydroxide ions are transferred to organic solvents in this fashion they are capable of reacting with metal carbonyl complexes, to produce highly-reactive intermediates. These can react with allyl derivatives to generate metal-allyl complexes.

It has been found in the present research that two products can be generated when $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{X}$ (where $\text{X} = \text{Cl, Br, I}$) is reacted with allyl bromide. As described previously, these complexes differ in the bonding arrangement of the allyl ligand. When the C_3H_5 moiety is bonded through a single bond, the compound

is referred to as a σ complex. Further complexation of the allyl double bond leads to the formation of a symmetric π complex. The relative yields of the σ and π complexes were found to be sensitive to a variety of factors including the nature of the halide ligand on the metal center, the rate and manner of addition of the reactants, the polarity of the organic solvent and the leaving group on the allyl reagent. These results suggest that two distinct mechanisms are operative for the selective formation of either σ or π complexes.

In order to investigate the effect of the metal identity on the products obtained in phase-transfer reactions, a series of ruthenium compounds were prepared. Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ with allyl bromide shows a strong preference for the production of the π -allyl complexes. This is in contrast to the reactions of the iron compounds where mixtures of σ and π products were obtained.

As a further comparison with the iron system, allyl cyanide was shown to react with $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Br}$ to form a π -allyl derivative, while no reaction was observed with the iron analogue. It is believed that the differences between the iron and ruthenium compounds are due to the ability of ruthenium to stabilize the intermediates responsible for the π -allyl formation. Additional work is needed in this area to confirm this speculation.

As noted above, the reactivity of metal complexes is sensitive to the identity of the ligand on the metal center. It is known that compounds of the type $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{olefin})$ undergo nucleophilic attack at the olefinic carbon. Such compounds have been found to be very useful in several organic syntheses. To examine the importance of the carbonyl ligands in such complexes, an effort was made to prepare analogous isocyanide-olefin complexes in which CNR groups are substituted for the CO ligands. Preliminary efforts on the synthesis of these compounds were unsuccessful but the experience gained indicates that the method is viable with minor modifications. Time limitations precluded further work on this system.

This research was directed towards the synthesis of metal derivatives with unusual structures and reactivities in order to explore their potential importance as precursors in organic synthesis. This research has confirmed the applicability of phase-transfer techniques to the synthesis of iron and ruthenium allyl complexes. It has further established those variables which can be used to optimize these syntheses. Exploration of the role of the metal center, the effect of ligands and the reaction conditions provide a foundation for continued research in this field.